

## Iridescent Hematite

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### **Abstract**

Iridescent hematite, also called rainbow hematite, displays a variety of beautiful interference colors. Usually, a thin film comprised of aluminum and phosphate was found to coat such hematite, although one example of a coating with aluminum and arsenate was discovered. The thin films that range from tens to hundreds of nanometers thick are believed to cause the color. High resolution secondary electron imaging shows that the thin film consists of nano-crystals arranged in three directions ( $120^\circ$  apart). The rod-shaped crystals have a width from 5 to 35 nm and display the same morphology on all samples irrespective if they are phosphate or arsenate. The composition of the bulk crystals coating the hematite have an Al to P atomic ratio that varies from 2.2 to 3.8. The minute crystals have failed to produce either an X-ray powder diffraction pattern, an electron back-scatter diffraction pattern, or a Raman spectrum.

**Key words:** Iridescent hematite, rainbow hematite, aluminum phosphate, aluminum arsenate, thin-film interference, nano-crystals.

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## Introduction

Occasionally, hematite is brilliantly colored with what appears to be a thin film on its surface that produces colors that range from solid and uniform to thin and resembling the interference colors of an oil slick. Such specimens with thin, iridescent coatings are frequently referred to as iridescent hematite. Sometimes, these iridescent specimens with thicker and brighter coloring have been referred to as 'turgite'. Formerly, turgite was considered to be a mineral that was comprised of a hydrated hematite, ' $\text{Fe}_2\text{O}_3 \cdot 1/2 \text{H}_2\text{O}$ '. Posnjak and Merwin (1919) argued that turgite was, instead, a mixture of hematite and goethite and Tochilin (1951) characterized turgite as a mixture of goethite, 'hydrogoethite' and 'hydrohematite'

In some cases, the iridescence is associated with dense, crystalline hematite; in other cases, it is associated with the surface of hard, botryoidal hematite or goethite. In the case of a 'rainbow hematite' currently in commerce, it is associated with a friable polycrystalline hematite that consists of a mass of weakly cemented hematite crystals that range from 10's to 100's of micrometers in width and up to a few tens of micrometers in thickness.

Numerous localities where iridescent hematite occurs have been documented and specimens from many more have offered for sale in commerce or illustrated on the internet. A sampling of significant reported localities includes: Bisbee, Arizona; Durango, Mexico; Cumberland, England; Diamond Hill, Rhode Island; Elba, Italy; Goldfield, Nevada; and Minas Gerais, Brazil.

The color has long been believed to be due to a thin coating, but the detailed identity of the coating has not been described. It is the purpose of this work to examine the origin of this highly visible and, at times, beautiful phenomenon.

## Experimental Details

Most of the samples investigated (Table 1) were chosen for obvious iridescent films on the surface of crystals or for what appears to be an obvious, strongly colored coating on the surface of the sample. The colors of the iridescent films are often reminiscent of the first and second order interference colors of oil slicks on water. Several of the samples were so brightly colored that, at first glance, they appeared to be coated with a uniformly colored phase over dimensions of several centimeters. For all of these samples, though, regions could be found where the colors showed gradational change into different colors on the surface of the sample.

A ZEISS 1550VP field emission scanning electron microscope (FESEM) with an in-lens detector was used for high resolution secondary electron (SE) imaging. Low voltage (< 5 kV) or 10 kV accelerating voltage imaging was performed on uncoated samples and carbon-coated samples. Low voltage SE imaging is important for studying morphology of nano-crystals due to smaller depth of beam penetration (Ma and Rossman 2006). An Oxford INCA 300 X-ray energy dispersive spectrometer (EDS) on the FESEM was used for elemental analysis at 10 kV in spot mode. Quantitative analyses were made with the XPP matrix correction procedure (Pouchou and Pichoir 1991). Electron back-scatter diffraction (EBSD) analysis of in-situ crystals at a nanometer scale were attempted using an HKL EBSD system on the FESEM, operated at 20 kV and 0.3 to 1 nA in a focused beam with a 70° tilted stage and a 5 to 10 mm working distance. Electron Microprobe analyses were obtained with a JEOL 8200 instrument at 15 keV and 30 nA with a 20 µm defocus beam mode. Standards used were hematite (Fe *Ka*), anorthite (Al *Ka*) and apatite (P *Ka*). The CITZAF matrix correction (Armstrong 1995) was employed for quantitative analyses. Raman spectra were obtained with a Renishaw M1000 system with 6 mW of 514.5 nm laser power at the sample. SIMS analyses were obtained on a Cameca 50L NanoSIMS. Standards were samples of synthetic berlinite (AlPO<sub>4</sub>), augelite (Al<sub>2</sub>PO<sub>4</sub>(OH)<sub>3</sub>), trolleite (Al<sub>4</sub>(PO<sub>4</sub>)<sub>3</sub>(OH)<sub>3</sub>). Infrared spectra were conducted with a Nicolet Magna 860 FTIR with a Continuum infrared microscope. Spectra were collected both with a microATR attachment and by direct transmission through individual coated hematite crystals. To reduce interference fringes, spectra of some crystals were obtained by placing the crystal on a thin KBr plate and coating the crystal with Halocarbon

Products Corp. fluorocarbon series 1.8 oil that is transparent in the 4000-2000  $\text{cm}^{-1}$  region.

To test the possibility that the phosphate is present not as an aluminum phosphate phase, but rather as an adsorbate on the surface of an aluminum compound, a series of exchange tests were conducted. Aliquots of a dark blue portion of sample 1462 were held at 35°C for 92 hours in solutions of 0.1 M  $\text{K}_2\text{HPO}_2$ , 0.1 M  $\text{KH}_2\text{PO}_2$ , 1.0 M  $\text{K}_2\text{HPO}_4$ , 1 M  $\text{HNO}_3$  and pure water. An additional sample was held at 98°C for 30 minutes in 1.5 M  $\text{HNO}_3$  to test both exchange and solubility of the nanocrystals.

## Results

### *FESEM studies*

Low magnification images show that individual crystals of hematite are coated with a thin film of material (Fig. 1). High resolution secondary electron imaging reveals that most iridescent hematite specimens examined have a surface film comprised of rod-shaped nano-crystals arranged in three directions (120° apart), as shown in Fig. 2. The rod-shaped crystals have a diameter from 5 to 35 nm. The thickness of the surface coating typically ranges from 200 nm to 500 nm. They are particularly well developed on hematite samples comprised of aggregates of individual, flat crystals.

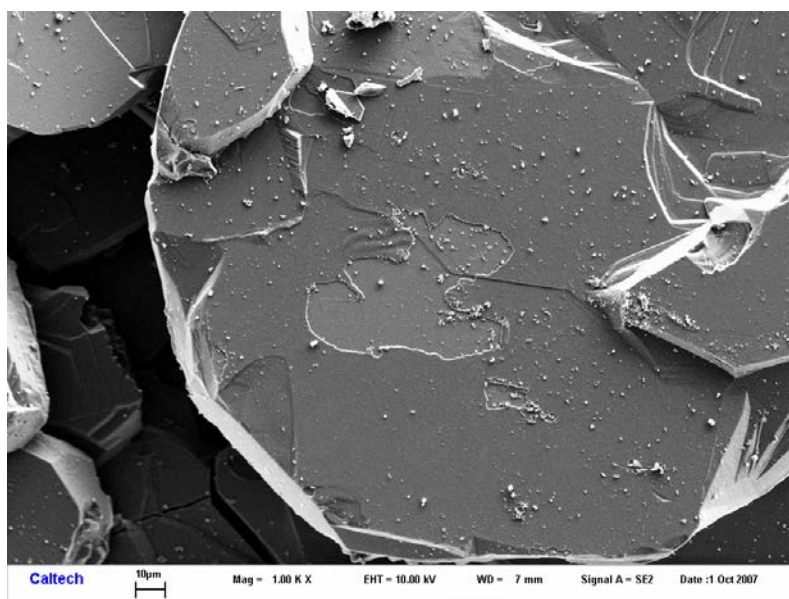


Figure 1. Low magnification image of GRR 1462 showing hematite crystals covered with a thin layer of aluminum phosphate. The larger crystal in the center has an area on the top side where the coating is missing.

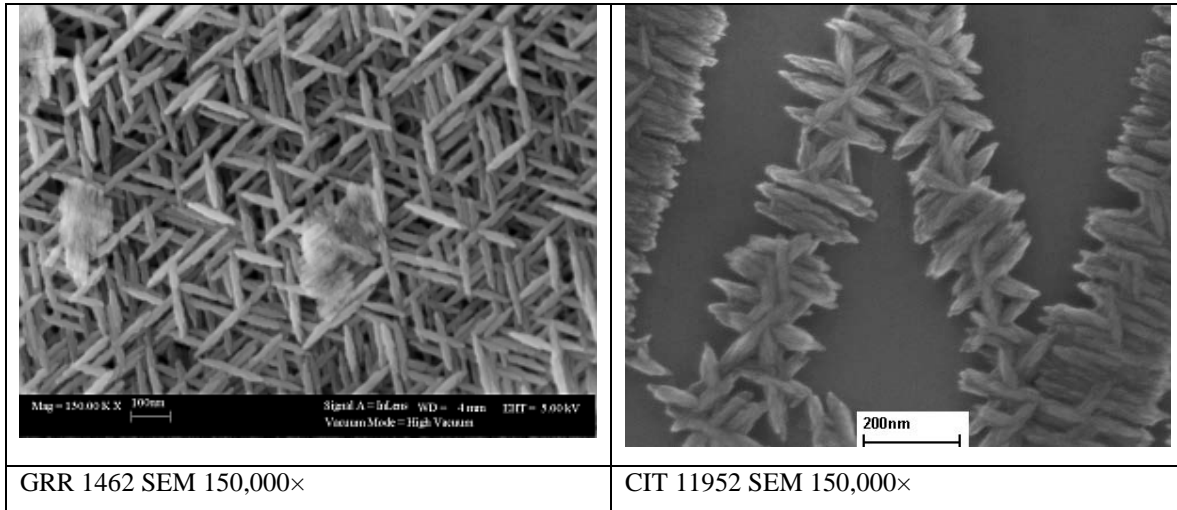


Figure 2. High magnification (150,000×) images of the aluminum phosphate crystals coating a single hematite crystal. A) A thick layer of aluminum phosphate crystals on sample GRR 1462; B) a thin, partially developed layer on sample CIT 11952.

Samples with botryoidal surfaces (e.g., GRR 2378, CIT-12889, GRR 1960) also have the nanocrystals on their surface. In these cases, the crystals are not a well ordered as in the case of the flat crystals, and they may form thicker, six-rayed clusters (Fig. 3).

The three comparison samples that had no evidence of iridescent colors showed no evidence for crystals or a foreign phase on the surface of the hematite. In particular, they did not display higher concentrations of either Al or P. This is in contrast to what was found for the samples with iridescence.

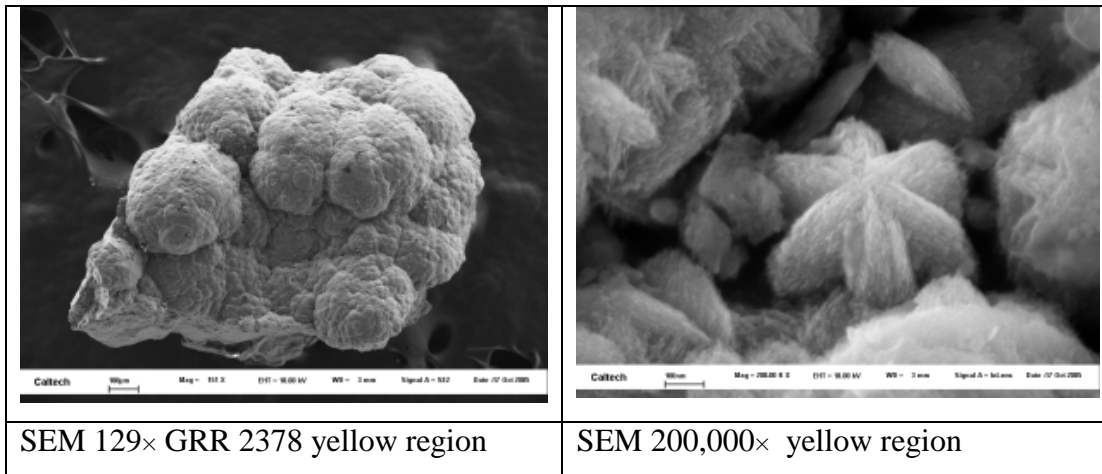
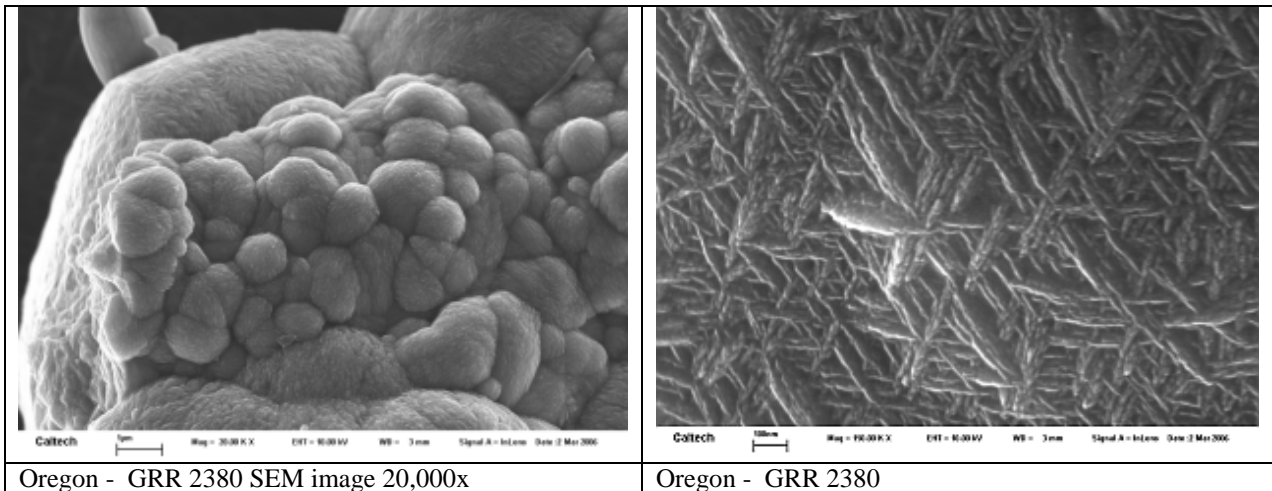


Figure 3. SEM images of the yellow region on iridescent hematite from Graves Mountain, Georgia (GRR 2378). Left: low magnification (129×) view of a fragment of the coating; right: high magnification view (200,000×) of the nanocrystals.

#### *EDS studies*

EDS analyses show that for most samples of iridescent hematite, the crystals coating the hematite contain aluminum and phosphorous (presumed to be present as phosphate). Among the samples the ratio of Al to P ranges from 2.21 to 3.47. Higher Al to P ratios (6.9 to 7.1) were observed with the Pico Mine sample (GRR 2377).

The primary exception was sample GRR 2380 from Quartz Mountain, Oregon, which had nano-crystals containing Al and As (presumed to be present as arsenate) covering hematite (Fig 4). The composition has Al and As in the atomic ratio of 1.98 to 3.03, with no P substitution of As.



Oregon - GRR 2380 SEM image 20,000x

Oregon - GRR 2380

Figure 4. SEM image of nanocrystals containing both aluminum and arsenic on hematite from Quartz Mountain, Oregon (GRR 2380). Left: 20,000 $\times$ ; right: 150,000 $\times$ .

#### *Electron Microprobe studies*

Electron microprobe analyses were obtained on 11 grains of GRR 1462 consisting of 35 distinct analytical points. All analyses of the surface layer were dominated by iron because the volume of excitation greatly exceeds the thickness of the coating. Al and P were in the 1 to 3 % range (as oxides). Other elements, such as Si, were absent. In a region of a hematite crystal with no visible coating, the  $\text{Al}_2\text{O}_3$  values fell to 0.1% and the  $\text{P}_2\text{O}_5$  values fell to 0.03% or less. The Al to P ratio is relatively constant for grains taken from a single hand specimen. For example, one sample has Al to P ratios that vary from 2.8 to 3.1. Individual colored zones from that sample vary slightly in the ratio: green (3.1), blue (3.1), deep blue (3.0), yellow-red (2.9). The Al to P ratios do vary from hand specimen to hand specimen. For example, grains from a different sample have Al to P ratios that range from 3.7 to 4.0. These ratios compare to 3.02, the grand average of all SEM-EDS analyses of GRR 1462.

#### *EBSD studies*

Several attempts to obtain EBSD analyses failed to capture a diffraction pattern due, most likely due to the small size of the nano-crystals. It is also possible that the nano-crystals are subject to decomposition under the SEM's electron beam. From the EBSD analyses, however, it is possible to determine that when the nano-crystals are

arranged on the (0001) surface of hematite, they arrange in three directions (Fig. 2b), as revealed by EBSD analysis on sample CIT 11952, where the nano-rods (120° apart) are parallel to the [10-10] [-1100] and [0-110] directions (i.e., the directions on the (0001) plane normal to {10-10} of hematite).

### *Raman Spectroscopy*

All attempts to obtain a Raman pattern from the coatings failed. Multiple accumulations of lengthy scans on GRR 1462 produced low-noise spectra, but did not reveal any features in addition to those of hematite. Likewise, low-noise spectra obtained on bare portions of the hematite that were subtracted from spectra of the coatings did not reveal features that arose from the coatings. In particular, no features from either carbonate or hydroxide were identified in the Raman spectra.

### *Infrared Spectra*

All infrared spectra of hematite crystals were dominated by an interference pattern that arose from the high refractive index of the thin hematite crystals. Spectra run under oil reduced the interference pattern to about half of its original intensity but did not eliminate it. Many, but not all, of the spectra showed a broad band under the interference fringes that maximizes at about 3160 cm<sup>-1</sup> (Fig. 5). When the average height of each interference band is plotted, the spectral pattern suggests that there are two overlapping bands, the stronger one at 3160 cm<sup>-1</sup> and the other at about 3495 cm<sup>-1</sup>. These are in the region where water and OH typically absorb. This is also a region where some AlO(OH) polymorphs absorb and most resembles the OH spectrum of boehmite. The spacings of the interference fringes in Figure 4, if derived from hematite, correspond to a thickness of 22 micrometers (assuming  $n_{\lambda}$  of 2.2 in the infrared OH region as modeled by Glotch et al., 2006) which is in the range of the measured thickness (7 to 25 μm) of typical crystals of sample 1492.

Unfortunately, due to the interference fringes, none of the spectra produced definitive results that would unambiguously demonstrate that OH was a part of the nanocrystals. The attempt to use microATR methods failed to produce a spectrum that differed from hematite.



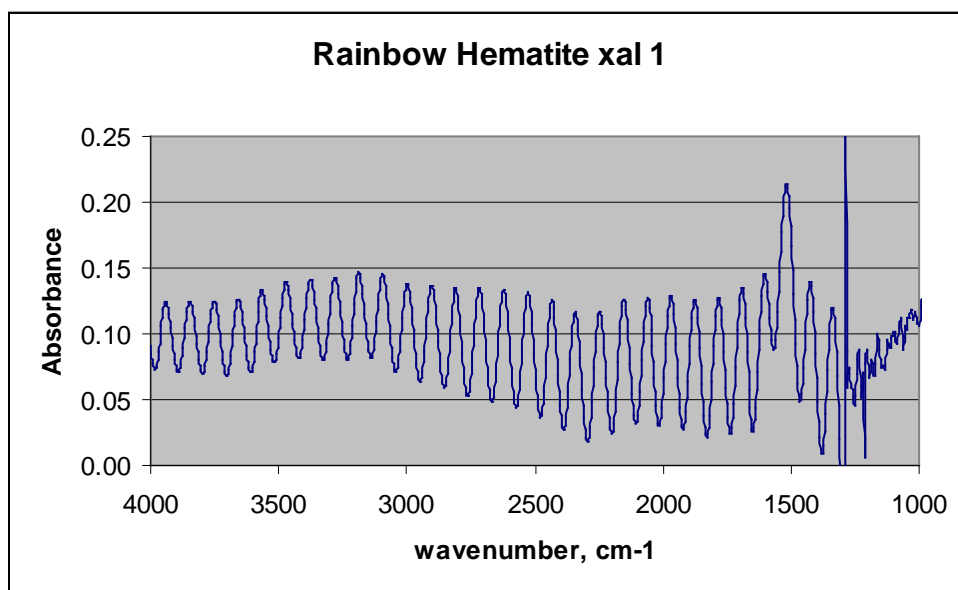


Figure 5. Transmission infrared pattern of a single flake of deep blue, iridescent hematite (GRR 1492) that shows an apparent broad band in the 3500-2800 cm<sup>-1</sup> region.

### *SIMS*

The atomic ratio of Al to P was determined for the calibration standards and on three grains of sample GRR 1462. The SIMS analysis confirmed that both Al and P were present in the coating, but gave higher Al to P ratios (8-14) than were obtained from either the SEM-EDS analyses of the SIMS sample or the electron microprobe and SEM-EDS analyses of other samples of GRR 1462. This is most likely due to differences between the sample (low density of packing of the nanocrystals) and the standards (dense crystalline material) and how they formed a plasma and were ionized. An SEM-EDS Al/P value of 3.45 was obtained on the sample of GRR 1462 used for the SIMS analysis.

### *Additional description of samples*

Nano-rods are not found on GRR 2522. This sample has brilliant colors on its surface that were particularly rich in the deep blue region. SEM and EDS analysis show that there are sub-micron layers of a different composition on the very surface of the sample. EDS analysis of surface layer reveals O, Fe, Al, Si, Cu. EDS analysis of the

underlying hematite gives only O and Fe. FeO(OH) occurs in valleys. A few micrometer-sized fluorapatite crystals are also found.

The crystals on the surface of the Pico Mine sample (GRR2377) displayed the oriented crystals approaching 400 nm in length, but also appeared to grade into stacks of plates that were about 15 nm thick and about 350 nm wide (Fig. 6). This is the sample with the highest Al to P ratio measured in this study.

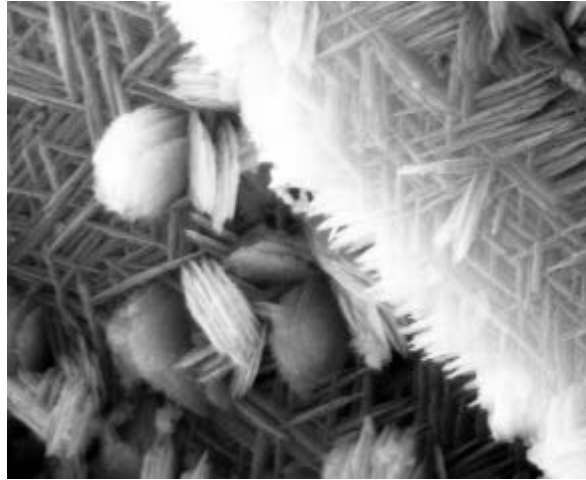


Figure 6. Crystals and plates on the surface of a green colored region of hematite from the Pico Mine (GRR 2377).

#### *Anion exchange tests*

The appearances of coatings do not change after 10 minutes immersion in concentrated hydrochloric acid, or by 30 minutes in 98°C, 1.5 M nitric acid. Likewise, samples recovered from the 92 hour, 35°C experiments with potassium phosphates and dilute acids showed no visually obvious change in color. The SEM images of these samples showed that the nanocrystals were still intact on all of the samples.

The Al content of the sample heated in 1.5 M HNO<sub>3</sub> for 30 minutes was lower (0.66 wt% Al<sub>2</sub>O<sub>3</sub> and 0.22 wt% P<sub>2</sub>O<sub>5</sub>) than the other samples from this locality that were analyzed in the electron microprobe (typically 2.5-3.0 and 1.1-1.5 wt% respectively), and the Al to P ratio was a higher (4.2). The color was not visibly changed by the acid treatment.

## Discussion

### *Origin of color*

Several observations indicate the color arises from interference effects. The color smoothly varies on the surface of some samples much the way the color of an oil film varies when on water of pavement. The color on a particular spot of a sample will vary somewhat depending on the angle of reflection. The layers of nano-crystals form thin films at a sub-micrometer scale that have an index of refraction which differs from hematite. In other mineral systems, crystals of sub-micrometer thickness and non-periodic layers of crystals and compositional differences at the sub micrometer scale have been show to cause interference colors (Ma et al. 2001, 2007). Thus, we conclude that the films cause interference colors in the iridescent hematite.

### *Mineralogy*

The Al to P ratio of about 3 to 1 observed for the layer on iridescent hematite does not correspond to any known crystalline phase. One phase that has an Al to P ratio of 3 to 1 may be evansite, an x-ray amorphous phase of possible composition  $\text{Al}_3(\text{PO}_4)(\text{OH})_6 \cdot 6\text{H}_2\text{O}$ . There is no obvious morphological difference between the crystals in the coatings containing aluminum and phosphate and the crystals containing aluminum and arsenate. In each case, the atomic ratios of Al/P and Al/As are generally of the same order. All our attempts to identify the nanocrystal phase have failed. The variable ratio of Al to P (or As) suggests that the nanocrystals may not be a single aluminum phosphate (or arsenate) phase.

From the infrared spectrum, an estimate of the water (or OH) content can be made. Assuming a density of 3.2 (intermediate between diaspore and boehmite) and a coating thickness of 300 nm on both sides of the hematite crystals, the absorbance in the OH region of about 0.042 gives about 2 wt%  $\text{H}_2\text{O}$  assuming a molar absorptivity of 100 for the OH region of the nanocrystals. Although there are many uncertainties with such a calculation, the calculation does not suggest that a stoichiometric hydroxyl phase is in the coating.

## *Genesis*

The development of the nanocrystals appears to be related to fluids that flow through the hematite. The color is developed on exposed surfaces, and on cracks or fractures in the hematite, or within highly porous samples such as GRR 1462. The orientation of the nanocrystals suggest that the nucleation of the crystals is templated by the hexagonal hematite structure on (0001) along the [10-10], [-1100] and [0-110] directions.

Not all iridescent hematites show the nanocrystals that contain aluminum and phosphate (arsenate) in SEM images. Three iridescent samples did not show these crystals in SEM images but, instead, were coated with other substances. CIT-12889 (Arizona) contained Na, Al, silicate and S in approximately the ratio of 0.2:0.3:1.0:0.1. CIT-14296 (Elba) contained Na, Al, silicate and S in the approximate ratio 0.4/0.9/1.0/0.2. GRR 2522 (Panamint Valley) contained Cu, Al, and silicate in highly variable ratios with minor amounts of P, S, As, Ca (e.g. Cu:Al:Si:P:S:Ca:As = 0.3:0.3:1:2.8:0.2:0.1:0.2)

In general, iridescent coatings on hematite are caused by thin (200 to 500 nm) coatings of other phases that have an index of refraction lower than the host hematite. In our studies, coatings of nanocrystals of a phase containing aluminum and phosphate were the most commonly observed. The ubiquity of these coatings suggests that the formation of these nano-phases is thermodynamically favorable process.

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**Table 1, Samples Examined**

Iridescent Hematite

Sample	Locality	Description
GRR 1462	Mina do Andrade, João Monlevade, Minas Gerais, Brazil	brilliant, variably colored polycrystalline friable, schist-like material
GRR 1960	El Salvador Mine, Sierra Mojada, Mexico	deep blue and green coating on a massive, fine-grained sample
GRR 2377	Pico Mine, Nova Lima, Minas Gerais, Brazil	thin coloration on a fracture surface of a hand-sized sample
GRR 2378	Graves Mountain, Lincoln County, Georgia, USA	intensely colored hand specimen with a brilliant play of colors
GRR 2380	Quartz Mountain, Douglas County, Oregon, USA	variably colored coating with strong greens
GRR 2522	Whittaker Iron Mine, Inyo County, CA, USA	strongly colored coating mostly in yellow, gold and red
CIT 11952	unspecified locality in Alaska, USA	thinly coated sample
CIT 12889	Dequesne, Santa Cruz County, Arizona, USA	moderately bright coating primarily in green but with smaller regions of other colors.
CIT 14296	Rio Marina, Elba Island, Livorno Province, Italy	thinly coated 8 to 12 mm crystals mostly lavender to blue color

Hematite with no evidence of iridescent coatings

CIT 2051	Bouse, La Paz County, Arizona, USA	5 mm crystals, specularite variety
CIT 8820	Broughton-in-Furness, Cumbria, UK	well-crystallized, 3-8 mm flakes on quartz
CIT 10446	Cherry Mine, Ishpeming, Michigan, USA	polycrystalline, approx 1 mm flakes, specularite variety.