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DETERMINATION OF THE OCCURRENCE OF GOLD IN AN UNOXIDIZED CARLIN-TYPE
ORE SAMPLE USING SYNCHROTRON RADIATION

by

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ABSTRACT

The occurrence of the so-called invisible gold in two unoxidized Carlin-type gold samples from Nevada have been determined using synchrotron x-ray fluorescence (SXRF) analysis at the National Synchrotron Light Source, Brookhaven National Laboratory. The samples were a bedded sample from the East ore zone of the Carlin deposit and a breccia sample from Horse Canyon. Preliminary results show that gold is found only in the Horse Canyon breccia sample. Experimental details including other x-ray line and diffraction peak interferences, standards used, and minimum detection limits (MDLs) are discussed.

To our surprise, and perhaps to many others who have studied similar Carlin-type unoxidized ore samples, gold was not detected in euhedral pyrite crystals except in the interior porous portion of one grain with MDLs of 0.8 to 3 ppm. Gold was detected in some parts of the matrix. The phase which contains gold has not yet been identified. The highest content of gold so far analyzed is about 40 ppm. Implications of these new findings are discussed.

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1. Introduction

The Carlin gold deposit, up in the Tuscarora Mountains of the Lynn mining district, about 35 km north of Carlin, Nevada, is one of the largest hydrothermal disseminated-replacement gold deposits in North America. Many other similar types of deposits occur in this district of Nevada. The Carlin deposit has produced over 4 million troy ounces of gold since 1965.

The Carlin-type gold ores are sometimes referred to as "invisible" gold because much of the gold is very fine-grained and does not occur as discrete free gold particles in unoxidized ore, and is therefore not visible under the optical microscope. Furthermore, because much of the minable gold ores contains 3 to 10 ppm gold in the whole rock, only analytical techniques with low minimum detection limits (MDLs) for gold can succeed in locating where and how the gold occurs and its abundance in the host mineral(s).

Previous investigators [1,2] have concluded that the gold occurs predominantly in pyrite in the unoxidized ores. Pyrite occurs in various forms such as framboids and subhedral to euhedral crystals, with grain size ranging from a few micrometers to crystals as large as 300 μm or more. Most of the pyrite crystals are less than 50 μm .

This paper describes the SXRF analysis [3,4] of euhedral pyrite crystals and the matrix of two unoxidized Carlin gold samples to determine the occurrence and abundance of gold in the samples. The main properties of synchrotron radiation that make it attractive for SXRF probe analysis are reviewed. Experimental details including other x-ray line and diffraction peak interferences, standards used, and minimum detection

limits are presented. Finally, the significance and implications of the new findings are discussed.

2.1 Carlin gold deposit

According to Radtke [2], the Carlin-type deposit is characterized by the occurrence of large ore bodies with very fine-grained disseminated gold in the upper beds of the Silurian Roberts Mountain formation. The host rocks for the ore bodies are fine-grained, dark to medium gray, thin-bedded siliceous, argillaceous, dolomitic limestones. Mineralogically the rocks are made up of large and widely varying amounts of calcite, dolomite, illite, and quartz, plus minor kaolinite, montmorillonite(?), chlorite, K-feldspar, plagioclase, pyrite, zircon, barite, rutile, sphene, and in the unoxidized ore, up to 0.5% carbonaceous materials.

Of the various deposits in this district, Carlin contains about 12 million tons of 10 ppm (0.32 ounce/ton) gold ores, Cortez contains 5 million tons of 7 ppm gold ores, the Jerritt Canyon deposit contains about 12 million tons of 7 ppm gold ores, and the most recent discovery at Gold Quarry, 26 km from Carlin, contains as much as 20 million tons of gold ores. Because of high gold prices, ores containing 3 ppm gold are being mined [5].

2.2 Sample selection and preparation

Two samples of unoxidized dark gray carbonaceous fine-grained ore was selected by W.C. Bagby for investigation by our combined method of SEM, EPMA, and SXRF. Sample 85RM-C-1 is a dark gray bedded silty limestone from the East ore zone of the Carlin deposit. Sample HCGS-2A consists of fragments of dark gray to black breccia from Horse Canyon.

in an acetone bath overnight until they floated free. Each polished wafer was then transferred and mounted on a mylar support 200 μm thick. The sample was positioned on the mylar so that it was centered over a 10 mm diameter circular hole which was cut in the mylar in order to allow the synchrotron beam to pass through the sample only, and not through any supporting substrate. A total of five wafers of the dark silty limestone sample 85RM-C-1 and three wafers of the breccia sample HCGS-2A were prepared for this experiment. The subsamples of 85RM-C-1 were numbered Carlin #1, 2, 4, 5, 6, and the subsamples of HCGS-2A were numbered Carlin #7, 8, and 10.

2.3 General mineralogy of the samples

Sample 85RM-C-1, the dark gray fine-grained carbonaceous silty limestone from the East ore zone, is a well bedded, porous, sedimentary carbonate rock with predominantly detrital calcite, scattered detrital quartz, small amounts of clay minerals, probably illite, and disseminated fine subhedral to framboidal particles of pyrite. Organic or carbonaceous fragments as large as 50 μm are extremely rare. Vienlets of calcite with a brown opaque mineral (not yet identified) without pyrite are abundant and represent the youngest event of fracture filling. Clusters and aggregates of coarser pyrite grains and masses occur in association with fracture-filling of calcite and quartz. They either cut across the bedding or are parallel to the bedding and are secondary in origin. A few scattered grains optically identified as sphalerite are also present.

Sample HCGS-2A, the dark gray to black fine-grained breccia, compared to the bedded silty limestone, is poorer in calcite and quartz, with fairly

in the horizontal plane and at 90° to the incident beam, the main background (which arises from incomplete charge collection in the detector from Compton and Rayleigh scattered photons) is minimized.

3.2 Apparatus

The incident synchrotron radiation beam was collimated by tantalum slits to obtain beam spots ranging from $20 \times 20 \mu\text{m}^2$ to $75 \times 75 \mu\text{m}^2$. Before impinging on the sample the beam was monitored by a helium ionization chamber. The samples were positioned at 45° to the incident beam with an X-Y-Z translational motor-driven target holder. Fluorescence x-rays produced in the sample were detected with a 30 mm^2 Si(Li) detector located 40 mm from the sample and at 90° to the incident beam. The detector was fitted with (i) a $300 \mu\text{m}$ silver collimator with a 3 mm diameter hole to restrict the x-rays to the center region of the detector, and (ii) a $200 \mu\text{m}$ Al filter to reduce the iron count rate from pyrite. The samples were viewed by a MTI TV camera attached to a horizontally mounted Nikon SMZ-10 stereozoom binocular microscope. Data acquisition and stepper motor control were performed with a Lecroy 3500 multichannel analyzer.

4. Data analysis

4.1 Other x-ray fluorescence line interferences with the gold lines

Figure 2 shows the gold region of the spectrum from a framboidal pyrite in the Carlin #6 sample using a $20 \times 20 \mu\text{m}^2$ incident synchrotron beam. Elements shown include copper, zinc, gallium, arsenic, selenium, lead, rubidium, and strontium. None of the major gold lines appears in the spectrum. If present, the $\text{AuL}\alpha_1$ line would have occurred 140 eV above the $\text{ZnK}\beta$ line, which is resolvable by the Si(Li) detector. The

of the peak at 9.712 keV, as seen in the bottom spectrum in figure 3, eliminates this possibility.

5. Analytical results

5.1 NBS lead standards

In the absence of a gold standard in pyrite or a matrix of calcite-quartz-carbonaceous materials, the $AuL\alpha$ counts were compared to the $PbL\alpha$ counts in NBS SRM 1874 K-490 (14700 ppm Pb) and NBS SRM 1875 K-497 (8600 ppm Pb). Differences in Z values were accounted for by using a calculated relative elemental sensitivity curve based on (i) the incident beam distribution, (ii) fluorescence cross sections, (iii) self-absorption, and (iv) the 200 μm Al filter fronting the Si(Li) detector.

Since each SRM represents a different glass matrix, use of the Pb standards introduces an unknown systematic error in the Au concentration levels presented below. The concentrations have been corrected for background only and not for any matrix effects.

5.2 Minimum detection limits

The running conditions were typically $t = 900$ seconds with beam spots of $20 \times 20 \mu m^2$; the measured MDL for Au was 3 ppm. For the large pyrite grains and the surrounding matrix, beam spots as large as $75 \times 75 \mu m^2$ were used, which lowered the MDL for Au to 0.8 ppm.

These SXRF MDLs for Au are lower than electron microprobe MDLs of several hundred ppm and PIXE MDLs of several ten ppm.

5.3 Gold concentration levels

To date we have examined 12 different pyrite grains, 3 carbonaceous

6 cases. There was no gold on the surface of one pyrite. For the runs where gold was detected, the gold may occur either in the matrix or on the surface of the pyrite.

3. Several organic-rich areas were analyzed, including a large area where the organic carbonaceous material is more clearly outlined. No Au was detected in the carbonaceous fragments or concentrated areas.

4. In many areas of the matrix of Carlin #7 and Carlin #10 analyzed with beam size from 50 x 50 to 75 x 75 μm^2 , gold was not detected. However, Au was identified and quantitatively measured in at least 9 areas within the matrix of Carlin #7 and Carlin #10. The maximum amount measured so far is about 40 ppm. As elsewhere in the sample, arsenic is an ubiquitous trace element present in all the runs.

5. The occurrence of Au detected at points in the matrix has a positive correlation coefficient of 0.69 with Zn, which means less than 2% probability that this is a chance event. The reverse however is not true, i.e., where there is Zn there may not be any Au. Correlation with Ga is -0.41 and with Rb -0.36, suggesting that the occurrence of gold is not correlated with minerals containing Al and K (Ga may substitute for Al, and Rb for K), such as illite, K-feldspar, or jarosite. At this time we do not know which phase contains the gold.

6. A small number of analyses were made on Carlin #6, which is from the dark gray fine-grained silty limestone. No gold was found either in a large framboidal pyrite grain, in the matrix, or in a massive pyrite area cut by veinlets of calcite and quartz. Because of the small number of analyses, we do not know where the gold is in this type of sample. Although no assay value of this specific sample was made, the estimated

dized ores of the Carlin-type is found in a paper by Hausen [7]. However, his experiment to recover gold from refractory unoxidized ore by oxidation is an indirect method that does not prove that the gold was originally in the pyrite. Hausen did not specifically show the presence of free gold in the oxidized pyrite. Another mineral phase containing gold could produce the same experimental results obtained by Hausen. In a similar study, Freeman et al. [8] also demonstrated that detection of fine gold particles may be enhanced by oxidation. Unfortunately, Freeman and others did not specifically state that the samples they studied are samples from the Carlin gold deposit.

Free gold particles have been identified in oxidized Carlin ores (Bagby, verbal communication, 1986) using SEM. The association of free gold with arsenic-bearing goethite suggests that the free gold was formed from arsenic-bearing pyrite. However, it is extremely difficult to prove whether the free gold is derived from pyrite or from the adjacent matrix.

In Hausen's unpublished thesis [9], study by electron microscopy clearly identified fine gold particles associated with quartz and clay from unoxidized Carlin-type ores. If much of the gold in the Carlin-type unoxidized ores is not in pyrite, then Hausen's earlier work deserves more attention.

We plan to obtain more synchrotron data on many types of unoxidized carbonaceous ores of the Carlin-type. In this way more definitive data on the precise occurrence or location of gold in such ores can be documented and understood.

Such data on the occurrence of gold, be it in pyrite or in other mineral phases in other samples, are data needed to reformulate our inter-

Cortez Gold Mines management for permission to publish the results of this investigation. This work was supported in part by the State University of New York/Geneseo (JRC), by the National Science Foundation (Grant No. EAR-8313683 to J.V. Smith, University of Chicago) (MLR and SRS) and by the U.S. Department of Energy, Division of Chemical Sciences (Contract No. DE-AC02-76CH00016) (ALH and KWJ).

Figure Captions

- Figure 1. Euhedral pyrite crystals from Carlin #7 sample. X100
- Figure 2. Region of the spectrum from the center portion of a 50 μm diameter framboidal pyrite where Au L lines would appear.
- Figure 3. Spectra from the "matrix" region of Carlin #7 breccia sample: top spectrum (275 μm Al in synchrotron beam), bottom spectrum (978 μm Al in synchrotron beam).
- Figure 4. Computer generated fit to the $\text{ZnK}\alpha$, $\text{AuL}\alpha$, $\text{HgL}\alpha$ and $\text{AsK}\alpha$ region of spectrum from a "matrix" region of Carlin #7 breccia sample.

NSLS14.45 CARLIN 6 H-1,1 FRAMBOIDAL PYRITE 20x20 μ m² BEAM
Time (sec) 964 Detector Si(Li) Aperture (mm) 3
Ion chamber 438 Slits (mm) .02,.02 Primary Filter 275 μ m Al
Energy (KeV) Filtered Distance (mm) 40 Detector Filter 200 μ m Al

NSLS14.40 CARLIN 7 E4 MATRIX

Time (sec) 902 Detector Si(Li) Aperture (mm) 3
Ion chamber 4020 Slits (mm) .07,.07 Primary Filter 275µm Al
Energy (KeV) Filtered Distance (mm) 40 Detector Filter 200µm Al

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