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The Effect of Collector's Type on Gold and Silver Flotation in a Complex Ore

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Gold and silver are recovered by gravity concentration, cyanidation, or flotation from ores. The choice of those processes depends on the mineralogical characterization as well as gold and silver contents of the ore. Flotation has been applied on ores containing free gold and silver particles for many years. The flotation efficiency of gold and silver particles depends on the modifiers and collectors. This paper presents the results of the effect of different collector combinations on gold and silver recoveries from lead and zinc ores by flotation. Best results were obtained on the use of Aero 208 + Aerophine 3418 A as collectors at the dosages of 350 + 350 g/t and 1000 g/t Na_2SiO_3 as a depressant at pH 4.5 where particle size was below 38 μm. According to the process, a concentrate assaying 1026.9 g/t Au and 10185 g/t Ag was obtained. On the other hand, a concentrate containing 50.6% Pb was obtained with 39.7% recovery using potassium amyl xanthate (KAX) and aminothiophenol (ATP). This concentrate graded 235 g/t Au and 3740 g/t Ag.

Keywords chelating reagent; flotation; gold; silver

INTRODUCTION

Gold and silver are usually found in native form or in the structures of sulphide and silicate minerals and as tellurides in nature. Today, precious metals such as gold and silver are usually recovered from metallic ores by chemical processes. Gravity concentration and flotation processes could be used prior to chemical processes depending on the ore formation (1–6).

Gold concentration processes usually consist of gravity separation, flotation, cyanidation, or a combination of these methods. The choice of those processes depends on the mineralogical characterization and gold content of the ore. In the case of high gold contents contains 250–300 g/t Au, alternative methods such as smelting for the treatment of the concentrate, other than cyanide leaching, may be viable (7,8).

Gravitational gold recovery has been developed significantly for the past twenty-five years, owing to the development of new gravitational techniques. Gravity concentrators such as spirals, shaking tables, Knelson, Falcon, Knudsen concentrators, and Multi-Gravity Separator have been effectively used in the concentration of finely liberated ores.

Free metallic gold can be recovered very effectively by flotation (1). The most common gold bearing sulphides are pyrite, arsenopyrite, and pyrrhotite. In the treatment of placer ores or gravity concentrates most gangue minerals are hydrophillic, and thus strong collectors should be used to maximize gold recovery with little concern for co-recovery of sulphides. This type of flotation is rare but has been proposed for low grade ores where gold is too fine to be recovered by selective flotation.

Fundamental concepts of gold and electrum flotation are considered, including the possibility of collectorless flotation of the minerals. This question is not yet resolved properly, but gold in some ores does float without collector (1,9). The hydrophobicity of gold and silver was enhanced by the addition of flotation collectors such as xanthates, dithiophosphates, and dithiophosphinates which are used in sulphide mineral flotation (1,10–14). The effect of copper activation and galvanic interaction on the behavior of free gold and refractory gold during froth flotation were studied by some researchers (15,16). Teague et al. also found that when copper sulphate is added after collector the recovery of free gold increases dramatically so that there is an overall increase in total gold recovery of up to 6% compared with the usual sequence of adding the copper first. On the other hand, studies have been carried out to find alternative flotation processing techniques for very fine gold and silver (17–19).

Ores of oxidized base metals such as Cu, Zn, and Pb may contain gold and silver. Different researchers have

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studied flotation of oxidized ores and suggested the following methods (20–27)

i. sulphidization followed by flotation with a sulphydryl collector, e.g., xanthates and activation by means of a metal ion,
ii. sulphidization using sodium sulphide followed by flotation with a cationic collector, e.g., amines,
iii. employing selective collectors such as mercaptants,
iv. using chelating agents.

The objective of this investigation is to explore the possibility of applying the flotation method to obtain marketable Au-Ag-Pb concentrates from an oxidized ore.

MATERIALS AND METHODS

Chemical Properties of the Ore Sample

The complex lead and zinc ore used in this study was taken from the Bolkardağ, Niğde region of Turkey. Chemical analysis of the representative ore sample is given in Table 1.

Chemical analysis showed that the representative ore sample contains 12.2 g/t Au, 256 g/t Ag, 3.45% Pb, and 3.15% Zn.

Mineralogical Properties of the Ore Sample

According to mineralogical studies, the representative ore sample contains primarily native gold, native silver, electrum, and argentojarosite as gold and silver minerals; cerusite, anglesite, galena, pyromorphite, mimetite, and plumbojarosite as lead minerals; smithsonite, hydrozincite, hemimorphite, adamite, and sphalerite as zinc minerals; limonite, hematite, goethite, pyrite, magnetite and siderite as iron minerals and quartz, feldspar, albite and muscovite as gangue minerals (28,29). Mineralogical analyses showed that the size of gold particles changed between 1 and 325 microns, and the average size was 12 microns. Electrum was determined to be between 5 and 35 microns. Furthermore, native silver particles having 5–35 microns particle sizes were observed inside galena and cerusite. The sizes of lead bearing minerals changed between 55 and 85 microns. Microscopic images of the minerals in the ore sample are shown in Figs. 1, 2, 3, and 4.

Flotation Tests

Flotation experiments performed with ore samples ground below 38 microns employing a Denver type flotation machine. During all flotation experiments, solids ratio was 20% and aeration rate in flotation cell was 10 L/minute. Combinations of aminothiophenol (ATP-C_6H_7NS) and potassium amyl xanthate ($CH_3CH_2CH_2CH_2CH_2OCS_2K$) as well as Aerophine 3418 A and Aero 208 were used as collectors, Na_2SiO_3 as a depressant, Na_2S as a sulphidizing reagent, and methyl isobutyl carbinol (MIBC) as a frother.

Aminothiophenol (ATP-C_6H_7NS) is a compound of aromatic thiol which is structurally analogous to phenol where hydroxyl group (-OH) bonded to the aromatic ring is replaced by a sulfhydryl group (-SH). Thiophenol is also

TABLE 1
Chemical analysis of the representative ore sample

Compound	Content
Au, g/t	12.2
Ag, g/t	256
Fe_2O_3, %	40.47
Pb, %	3.45
Zn, %	3.15
Cu, %	0.11
SiO_2, %	29.09
MgO, %	0.81
CaO, %	3.53
Al_2O_3, %	3.01
Na_2O, %	0.09
K_2O, %	0.56
TiO_2, %	0.14
P_2O_5, %	0.10
MnO, %	1.24
Loss on Ignition, %	13.90

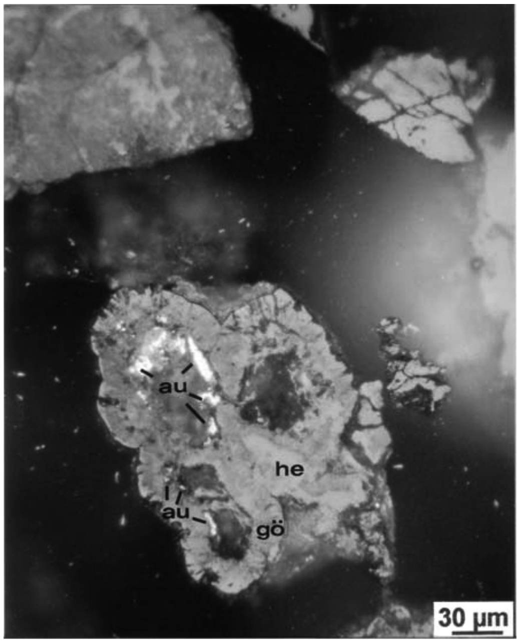


FIG. 1. Native gold particles (au) in hematite (he) and goethite (gö).

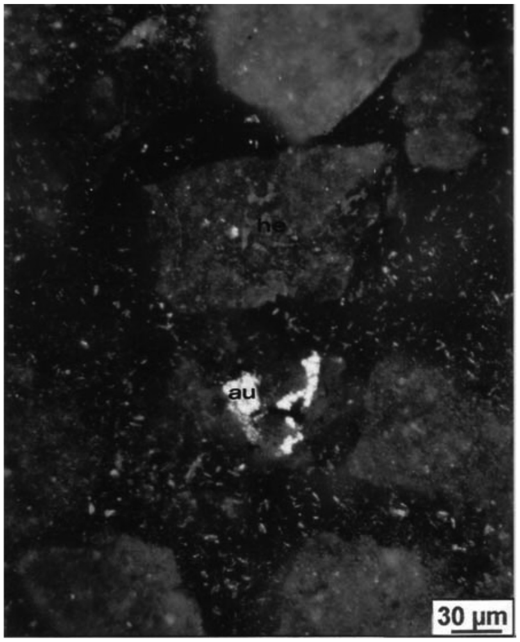


FIG. 2. Native gold particles (au) in hematite (he).

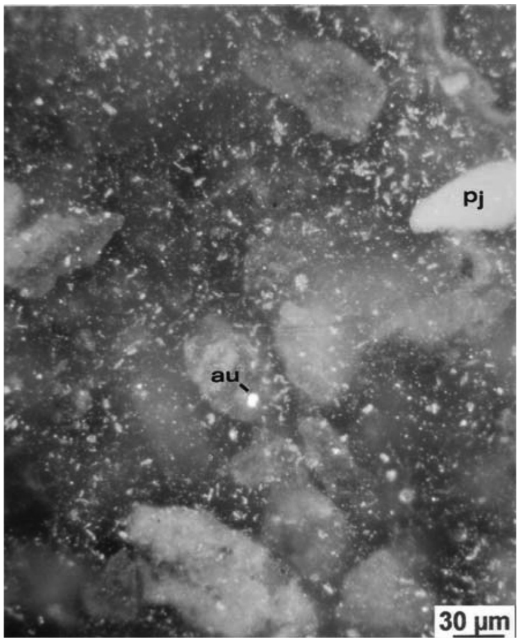


FIG. 4. Native gold (au) particles together with cerusite (se), mimetite (mi) and plumbojarosite (pj) particles.

called phenyl mercaptan. Thiophenol is a toxic, flammable, clear liquid with a strong and unpleasant odor; boiling at 168°C. It is insoluble in water but soluble in alcohol and ether. Many chemical reactions of thiophenols are analogous to phenols. The substantial difference between sulfur and oxygen is that sulfur much more readily gets oxidized to higher oxidation states than oxygen. Thiophenols can form thiophenolate anions by losing sulfhydryl H^+ ions; used as reagents for the simple chemical preparation. The ring closure reaction of *o*-amino thiophenol produces benzothiazole, an important industrial product. Thiophenol itself is used as an antinematodal agent. Thiophenol class compounds have the skeleton of thiophenol.

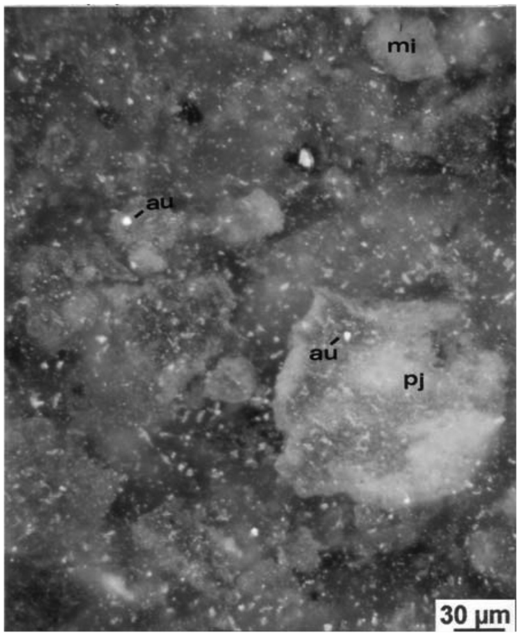
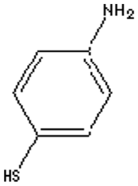
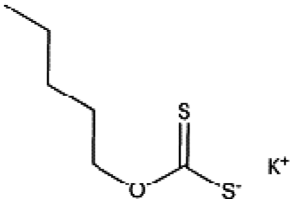


FIG. 3. Native gold (au) particles together with cerusite (se), mimetite (mi) and plumbojarosite (pj) particles.



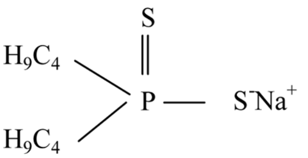
(1)

As is well known, xanthates can be obtained by reacting an alcohol with carbon disulphide and an alkali such as sodium hydroxide or potassium hydroxide. The alcohols employed are not unique. They can form ethyl, butyl (isobutyl, normal butyl, secondary butyl), propyl (isopropyl, normal propyl), and amyl (isoamyl, normal amyl, secondary amyl) xanthates, in dry forms, such as powder, granules, pellets, tablets, or flakes. Xanthate is the common name for chemical reagents used in the flotation of base and precious metals, which is the standard method for separating valuable minerals, such as gold, copper, lead, or zinc minerals, from non-valuable minerals, such as limestone or quartz (gangue). The most common xanthates added to flotation circuits are ethyl and amyl xanthates (30).



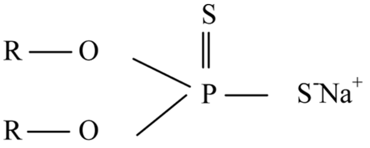
(2)

Aerophine 3418 A promoter is a unique, P-based sulfide collector. It was originally developed for the flotation of copper and activated zinc minerals. It has since been found to be an invaluable (and often irreplaceable) collector in the beneficiation of complex, polymetallic, and massive sulfide ores. On these ores it provides very selective separations. It is highly effective for galena and precious metals, especially silver. Its main attributes are strong collecting power but with excellent selectivity against iron sulfide minerals, inactivated sphalerite, and penalty elements. On many ores, the dosage required may be considerably lower than that needed for traditionally-used non-selective collectors such as xanthates.



$$\begin{matrix} H_9C_4 \\ H_9C_4 \end{matrix} > \overset{\overset{S}{\|}}{P} — S^-Na^+ \qquad (3)$$

Aerofloat 208 promoter is used mainly for selective flotation of Cu from Cu/Zn ores where Zn minerals tend to float readily; for flotation of activated Zn sulfides where selectivity against iron sulfides presents a problem. It is very selective against iron sulfides. Besides it is used as an excellent collector for native Au, Ag, and Cu.



$$\begin{matrix} R—O \\ R—O \end{matrix} > \overset{\overset{S}{\|}}{P} — S^-Na^+ \qquad (4)$$

RESULTS AND DISCUSSION

Flotation Experiments Performed with ATP-KAX Combination

Representative ore sample was ground under 38 microns particle size prior to multi stage flotation experiments where 600 + 600 g/t ATP + KAX combination were used. While natural pulp pH was 8.5, it increased to 9.85 by the addition of Na_2S. Experimental conditions, experimental flowsheet and combined results are given at Table 2, Fig. 5 and Table 3, respectively.

TABLE 2
Flotation conditions for ATP+KAX combination

Na_2SiO_3	1000 g/t
Na_2S	5600 g/t
ATP	600 g/t
KAX	600 g/t
MIBC	40 g/t
Na_2SiO_3 Conditioning Time	10 minutes
Na_2S Conditioning Time	21 minutes
ATP+KAX Conditioning Time	40 minutes
Flotation Time	20 minutes
Cleaning Stages Conditioning Times	6 minutes
Cleaning Stages Flotation Times	15 minutes

As it is seen from Table 3, a concentrate assaying 50.6% Pb was obtained with 39.7% recovery. The concentrate was found to contain 235 ppm Au and 3740 ppm Ag. Test results suggested that KAX and ATP were highly effective on the flotation of gold and silver associated with oxidized lead minerals.

Flotation of zinc minerals in the ore could not be achieved using the combination of ATP + KAX in contrast to the reports in the literature (11,23). This is likely because of the very complex mineralogical structure of the ore owing to the oxidized iron and zinc minerals. On the other hand, gold and silver minerals in the ore were successfully floated using ATP and KAX as collectors although it is known that ATP is particularly effective on oxidized lead-zinc minerals. When xanthate was used alone in the flotation, 15% of Au and Ag minerals could be floated;

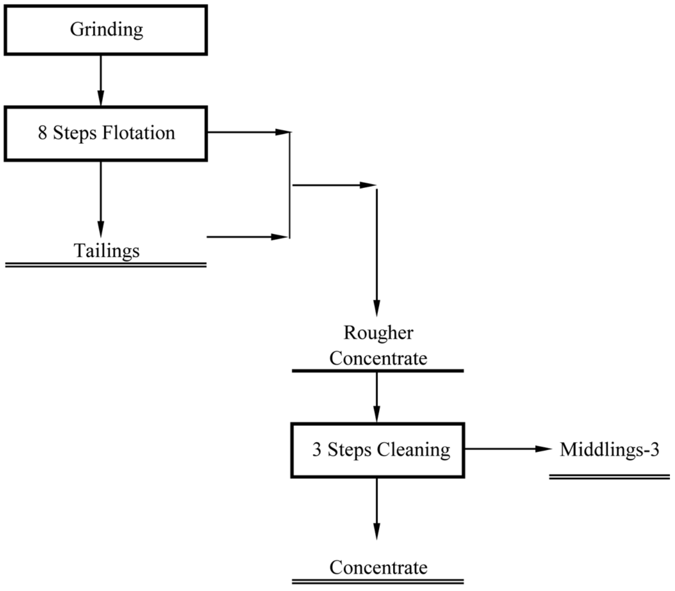


FIG. 5. Experimental flowsheet for ATP+KAX combination.

TABLE 3
Results of experiments performed with ATP+KAX combination

		Au		Ag		Pb	
Products	Weight %	Content, ppm	Recovery, %	Content, ppm	Recovery, %	Content, %	Recovery, %
Concentrate	2.7	235.0	52.5	3740	37.6	50.60	39.7
Tailings	97.3	5.9	47.5	172	62.4	2.13	60.3
Total	100.0	12.1	100.0	268	100.0	3.44	100.0

however, in the case of ATP + KAX combination, 52% of gold and 32% of silver could be floated. These findings suggest that ATP is also effective on Au and Ag minerals.

Where reagents of the ATP type are concerned, these exert chelating action towards Pb and Zn. Chelating occurs through a weak dative bond of the nitrogen and the saline bond of –SH (22,31,32). Since the collecting action of chelating reagents is directed towards the cation present on the mineral surface, irrespective of the mineralogical class, it is expected that these reagents achieve flotation of zinc, lead, minerals either oxides or sulphides in the same way, i.e., it seemed logical that, by the use of a suitable chelating agent, it might well be possible to remove the barrier between base-metal sulphide and oxide minerals, which do not respond equally to the same conventional collectors.

Flotation Experiments Performed with Aerophine 3418A-Aero 208 Combination

The combination of Aerophine 3418A (200 g/t) and Aero 208 (Cytec Ind.) (200 g/t) was used in the flotation experiments. These are dialkyl dithiophosphate type reagents which are especially used for the flotation of native gold and silver.

Ore sample was ground under 38 μm prior to multi-stage flotation experiments. Flotation test conditions, experimental flowsheet and results are given in Table 4, Fig. 6 and Table 5, respectively.

It can be seen from Table 5 that the Aerophine 3418A + Aero 208 combination more effectively floated the gold and silver compared to the oxidized lead minerals as expected. Studies on the interactions of gold and silver with collectors such as xanthates and dithiophosphates are considered as a guide to practical flotation. It has been shown that xanthates adsorb on gold and silver by electrochemical reactions involving xanthate species where oxygen must exist.

Non-conventional collectors i.e., collectors different to xanthates are frequently used in the sulphide flotation practice. An example of non-conventional collectors is sodium-di-isobutyl dithiophosphinate (DTPINa), known under the trademark of Aerophine 3418A of Cytec Industries. DTPINa is mainly recommended to float lead, copper, and precious metals from minerals containing high levels of pyrite, as is the case of polymetallic ores.

Research works on froth flotation of sulfides in the presence of non-conventional collectors (e.g., thiophosphinates, thionocarbamates, etc.) have demonstrated that the selective activation of the mineral species is substantially affected by the electrochemical conditions (pulp potential) of the flotation slurry (33,34). Despite very little fundamental

TABLE 4
Experimental conditions for Aerophine 3418A+Aero 208 combination

Na_2SiO_3	1000 g/t
Aerophine 3418 A	200 g/t
Aero 208	200 g/t
Na_2SiO_3 Conditioning Time	10 minutes
Aerophine 3418 A+Aero 208 Conditioning Time	20 minutes
Flotation Time	10 minutes
Cleaning Stages Conditioning Times	4 minutes
Cleaning Stages Flotation Times	10 minutes

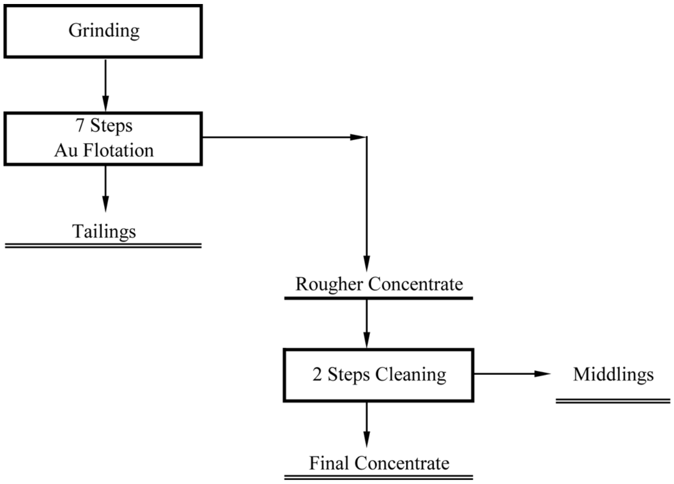


FIG. 6. Experimental flowsheet for Aerophine 3418A-Aero 208 combination.

TABLE 5
Results of experiments performed with Aerophine 3418A+Aero 208 combination

		Au		Ag		Pb	
Products	Weight %	Content, ppm	Recovery, %	Content, ppm	Recovery, %	Content, %	Recovery, %
Concentrate	0.7	920	51.1	10100	31.2	11.38	1.4
Tailing	99.3	6.2	48.9	180	68.8	3.12	67.4
Total	100.0	12.6	100.0	259	100.0	3.21	100.0

data are available on the electrochemical response of sulfides in presence of DTPINa. It is known that the interaction mechanism of different thiol collectors with sulfides is essentially similar. However, examinations of non-conventional collectors such as thionocarbamates and hydroxamate (35,36) have revealed some differences with regard to the xanthates. For example, a chemisorption process (with no electron transfer) that proceeds at lower potentials compared with the potentials at which the electrochemical adsorption of xanthates occurs. According to Basilio and Yoon (35), this behavior is due to the small pK of the corresponding metal–collector compound. Although it is believed that DTPINa interacts with sulfides through mechanisms analogous to those accepted for xanthates, thus far it has not been demonstrated. According to the above, knowledge of the interaction mechanism of DTPINa with common sulfides might contribute to the basic understanding of sulfide flotation chemistry (37).

CONCLUSIONS

According to the mineralogical studies, the representative ore sample contains primarily native gold, native silver, electrum, and argentojarosite as gold and silver minerals; cerusite, anglesite, galena, pyromorphite, mimetite, and plumbojarosite as lead minerals; smithsonite, hydrozincite, hemimorphite, adamite, and sphalerite as zinc minerals; limonite, hematite, goethite, pyrite, magnetite, and siderite as iron minerals, and quartz, feldspar, albite, and muscovite as gangue minerals.

A concentrate assaying 235 ppm Au, 3740 ppm Ag and 50.6% Pb was produced as a result of 7 stages flotation experiments performed with ATP + KAX collector combination below 38 µm particle sizes. The optimized conditions were 5000 g/t Na_2S, 1000 g/t Na_2SiO_3, 600 g/t KAX and 600 g/t ATP.

A concentrate containing 920 ppm Au, 10100 ppm Ag, and 11.38% Pb was produced as a result of 7 stages of flotation experiments performed with Aerophine 3418A + Aero 208 collector combination below 38 µm particle sizes. The optimized conditions were 1000 g/t Na_2SiO_3, 350 g/t Aerophine 3418A + 350 g/t Aero 208.

In the case of ATP + KAX combination, Pb floated more efficiently compared to Aerophine 3418A + Aero 208 combination. This finding reveals the chelating power of ATP on oxidized Pb minerals. This study proves that the flotation of oxidized minerals could be achieved with chelating collectors which have a strong affinity for metal cations of the mineral surface as reported by Somasundaran and Nagaraj (20) and Marabani, et al. (22). ATP is also seen to be effective on gold and silver minerals where an ATP + KAX combination is used as a collector.

Gold is found in the form of native and electrum in the ore while silver is generally seen as argentojarosite though a minor amount of native silver is observed. The reason for the gold recovery being higher than silver is due to the existence of argentojarosite (38).

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