A REVIEW ON THE MINERALOGY OF STIBNITE IN HYDROTHERMAL GOLD DEPOSITS

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Abstract: Stibnite is an important mineral in hydrothermal gold mineralization systems. The study of stibnite mineralogy is an integral part of the study of the mineralization mechanism of hydrothermal gold deposits. The mineralogical characteristics of stibnite mainly include physical structure and chemical composition characteristics. The author reviews the morphology, unit cell parameters, infrared spectrum, electron paramagnetic resonance spectrum and other physical characteristics of stibnite in hydrothermal gold deposits, as well as rare earth trace elements, The geochemical characteristics of sulfur isotopes, the application of antimony isotopes, the gold content of stibnite in hydrothermal gold deposits, and many other aspects.

Keywords: Stibnite mineralogy; Physical and chemical characteristics; Antimony isotope; Hydrothermal gold deposit

1 PHYSICAL STRUCTURAL CHARACTERISTICS OF STIBNITE

About 80% of global gold reserves come from hydrothermal gold deposits. With the continuous in-depth research on typical hydrothermal gold deposits in recent years, the mineralization theories of various gold deposits have been continuously improved, and a large number of research results have continued to emerge. However, there are many classifications of hydrothermal gold deposits, the geological characteristics of each deposit are quite different, and the ore-forming geological processes are complex. The more recognized types of hydrothermal gold deposits are mainly porphyry type, epithermal type, There are several types such as Carlin type, orogenic type, finely disseminated type, and gold deposits related to intrusive rocks. The mineral combination characteristics of these types of gold deposits are relatively complex. The common metal minerals produced by the deposits mainly include pyrite, arsenopyrite, galena, sphalerite, antimony, natural gold, chalcopyrite, and bornite. , sulfur-arsenic copper ore, various silver minerals, etc., the elemental composition is mainly sulfur-loving elements.

Stibnite, as one of the more commonly produced sulfides in hydrothermal gold deposits, has important value in the research of this type of deposits. Stibnite is commonly produced in orogenic gold deposits, Carlin-type gold deposits, and fine disseminated gold deposits [1-2].

Through the mineralogy study of stibnite, important information on the mineral deposits and fluid sources, the origin of the deposits, and the metal precipitation mechanism can be obtained, and it has become an important field of research on the mineralization of gold deposits [3-6].

1.1 Morphological Characteristics of Stibnite

Antimonite crystals are sulfide minerals of the orthorhombic crystal system. The unit cell parameters are a0=11.20nm, b0=11.28 nm, c0=3.83 nm; the main component of the crystal is a chain composed of sulfur ions and antimony ions that are parallel to the C axis and closely connected. The sulfur and antimony ions on the same chain in the crystal The distance between ions of the antimony element is small, about 2.5 nm, and the bonding force between ions is strong; but in the crystal, the distance between sulfur and antimony ions between different chains is larger than the distance between the same chain. Around 3.2nm, the bonding force between ions is weak, which makes it possible for some other elements to be mechanically mixed into the crystal. This is also the reason why stibuite is often mixed with a small amount of other impurity elements [7].

The common morphological characteristics of stibnite crystals are easy to distinguish. Single crystals are often long columnar or needle-shaped, with obvious vertical lines on the columnar surface, and are mostly conical along the long axis. The ones produced in the wild are generally in the form of needle-shaped, radial, columnar or massive aggregates with strong metallic luster. The color is mainly lead gray or steel gray, with black and gray streaks.

In gold deposits, the common crystal forms are mainly in the form of other-shaped granular, microgranular, dense massive aggregates, veinlets, semi-euhedral plates, columns, radial, hair-like, etc. After the formation of mineral crystals, affected by the later tectonic stress, some mineral crystals can be seen under the microscope as bending, twisting and deformation, and wedge-shaped lamellar twin crystals appear. In the Lannigou gold deposit in Guizhou [8] and Sandu in Guizhou The stibnite in the Miaolong gold-antimony deposit [9] all shows microstructural deformation characteristics.

In gold deposits, changes in the composition of the heated fluid and the geological environment will also cause corresponding changes in the stibuite crystal structure. Danilo conducted in-depth research on stibuite of different origins, compared the unit cell parameters of stibuite formed under different temperature conditions, and confirmed that there is a clear correlation between the formation temperature (T) of stibuite and the unit cell parameters. Property (Figure 1).

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The unit cell parameters of stibnite have a negative correlation with the mineral formation temperature, that is, the unit cell parameters decrease as the formation temperature increases. Qin Shan , Liu Yingjun , He Mingyue , Quan Shaolong et al. respectively studied the Lejiawan antimony deposit in northern Guangdong, the Woxi and Longshan antimony-gold deposits in Hunan, the tin mine in Hunan, and Daxing in Heilongjiang[10-13]. Similar relationship characteristics were also found in the study of stibnite in Tun antimony gold. This proves that a large value of the unit cell parameter a is a significant typical characteristic of low-temperature gold-bearing antimonyite.



1.2 Infrared Spectrum

Peng Wenshi et al. studied and obtained that the highest frequency and characteristic absorption peak of stibnite is 334cm-1 in the wave number range of $300 \sim 1600$. When Liu Yingjun et al. studied low-temperature gold-bearing stibnite, they found that the infrared absorption band of stibnite can be roughly divided into three areas [14-15]: ① The highest frequency band and characteristic peak area: 337 cm-1, which is a relatively Strong sharp absorption band; ② The strongest absorption area is in the range of 300 to 200 cm-1, consisting of a strong band (242cm-1) and 2 to 3 weak bands (272cm-1, 220cm-1). The absorption bandwidth is Strong; ③ The medium-strength absorption zone is in the range of 200 to 100cm-1, mainly composed of 5 to 6 medium-strength absorption bands, forming obvious double-peak characteristics at 185cm-1.

1.3 Electron paramagnetic Resonance Spectrum

Electron paramagnetic resonance spectrum of low-temperature gold-bearing antimonyite

(EPR spectrum) has a structure with the same isotropic properties, and the g factor of this structure is 2.0015 (\triangle H=2.5 Gauss), while the electron paramagnetic resonance spectrum of gold-poor antimonyite under medium temperature conditions does not have such a fine structure; When the same antimonite sample is tested for electron paramagnetic resonance spectrum, the spectral line characteristics of the sample will change with the test temperature. When the temperature is lowered from room temperature to 110K (-163 °C), the relative electron paramagnetic resonance single spectral line of the sample will The intensity is significantly enhanced [16].

2 CHARACTERISTICS OF CHEMICAL COMPOSITION OF STIBNITE

The chemical composition of stibnite is Sb2S3, with an antimony content of 71.4% and a sulfur content of 28.6%. Because of its low crystallization temperature (mostly around 200°C), it is commonly found in low-temperature hydrothermal deposits, often symbiotic with quartz, calcite, orpiment, realgar, pyrite and other minerals. As a product of hydrothermal activity, stibnite in nature is often mixed with impurity elements such as As, Ag, Cu, Fe, Pb and a small amount of rare earth elements during the formation process; antimony and bismuth elements can form antimony-stibnite at room temperature. Bismuthite is a continuous homogeneous material, but under geological conditions, only bismuthite antimonite (Bi, Sb) 2S3 is found in this series, and its composition contains antimonite-bismuthite content from 9:11 to 13:7.

2.1 Rare earth Element Geochemistry

Stibnite generally contains low rare earth elements ΣREE (excluding Y element, the same below), such as the Bameng antimony deposit in Guizhou and the Yangshan gold deposit in the West Qinling [6]. The main reason is that antimony element is a sulfur-loving (copper) element, which mainly forms sulfide or sulfate minerals during geological processes; rare earth elements (REE) are mainly lithophile elements and are easy to form oxides, carbonates, and phosphates. Minerals, therefore, rare earth elements and antimony elements have been separated during geological processes. At the same time, the atomic radius, covalent radius, and ionic radius of antimony and sulfur elements are smaller than those of rare earth elements. At the same time, they are affected by various factors such as radius and electronegativity, making it difficult for rare earth elements to enter the antimony crystal lattice, resulting in antimony The content of rare

elements in the mine is low. In fine disseminated gold deposits (spots), due to the influence of geological processes, the content of rare earth elements in stibuite changes relatively greatly, while the material source of large gold deposits is relatively stable, and the content of rare earth elements in stibuite is generally between 11.628×10 Between $-6 \sim 26.617 \times 10-6$.

The content of light rare earth Σ (La-Nd), medium rare earth Σ (Sm-Ho), and heavy rare earth Σ (Er-Lu) elements in stibnite varies greatly, accounting for approximately 65% to 99% of the total Σ REE, respectively. 0.9 ~ 20.2%, 0.1% ~ 8.0%, showing the characteristics of Σ (La-Nd) > Σ (Sm-Ho) > Σ (Er-Lu), obviously rich in light rare earth elements, and poor in heavy rare earth elements. Rare earth partitioning patterns. The stibnite light rare earth element Σ (La-Nd) in gold deposits is more abundant, accounting for more than 83% of the total rare earth elements. The LREE/HREE ratio in gold-rich stibnite is relatively high, while the LREE/HREE ratio in gold-poor stibnite is relatively low, indicating that light rare earth elements are relatively enriched in gold-poor stibnite, while heavy rare earth elements are present in gold-poor stibnite. elements are relatively high. Stibnite is not the main carrier mineral of rare earth elements. The content of rare earth elements in antimony in different types of deposits varies greatly. The content of rare earth elements is generally higher than that in gold-free antimony. The content ratio of light to heavy rare earth elements. Using the rare earth elements of stibnite (La/Sm)N-(La/Yb)N-(The La/Lu)N triangle diagram can roughly distinguish gold-bearing and gold-poor stibnite, and whether the sample comes from antimony deposits or finely disseminated gold deposits.

2.2 Isotopes

The sulfur isotope composition reflects the source of mineralization materials and the isotope fractionation caused by the mineral formation process. Generally speaking, sulfur in the upper mantle is the birthplace of sulfur in the earth's crust. The causes of sulfur in metal deposits are mainly divided into primary sulfur and crustal sulfur. , mixed sulfur type III[11].

The sulfur isotope characteristics in gold mines are affected by many factors, and most of them have similar characteristics to pyrite, arsenopyrite and other sulfides produced in the same area. Ai Guodong et al., in their study of gold deposits in Hunan Province, found that the δ 34S values of the sulfur isotope composition of gold-loaded sulfur (arsenic) compounds are concentrated within a range of \pm 5‰ deviating from the "zero" point, and vary from Large negative values are dominant. When Bao Zhenxiang studied the gold deposits in the Jiangnan ancient island arc belt, he analyzed the S isotopes in pyrite, arsenopyrite, and stibnite in 14 gold deposits and found that most of the sulfur isotope δ 34S values in this area were also deviating from Around \pm 5‰ near the "zero" point, the composition is relatively stable, the range of change is small, and the symbiotic sulfur (arsenic) compound isotopes have basically reached balance[3, 12].

Stibnite is the main form of mineral output containing antimony elements. In recent years, with the gradual in-depth research on antimony isotopes, antimony isotopes have unique advantages in environmental pollution and archaeological research. With the in-depth study of its fractionation mechanism and the expansion of its application range, By extension, antimony isotope research is also used in geosciences. Degao Zhai et al. found through research on stibnite in tin mines that the formation process of antimony will lead to significant Sb isotope fractionation, and the light antimony isotope (121Sb) is more likely to precipitate than the heavy antimony isotope (123Sb). Ores, stibnite ores precipitated away from fluid sources will gradually have higher Sb isotope compositions, suggesting that Sb isotopes can be used to indicate the direction of hydrothermal flow. Sb isotopes can therefore be used to identify hydrothermal flows and reveal different processes in natural systems[7].

2.3 Elemental Geochemistry of Stibnite

During the crystallization process of antimony, there are many main element vacancies, allowing other elements to enter it. Some of the antimony element vacancies are replaced by bismuth, lead, zinc, copper, iron and other elements, and part of the sulfur element is replaced by arsenic and selenium elements, making it The antimony content in stibuite is less than the theoretical chemical composition value of stibnite (71.4%). The content of antimony, the main element of stibnite in gold deposits, is mostly between 66.53% and 70.88%, and the sulfur content is mostly between 26.77% and 29.71%. During the period, most antimony ores contained less than 70% antimony and less than 28.2% sulfur. The Sb and S weight percentage values of gold-bearing stibnite in the same deposit are generally relatively stable. For example, in the tungsten antimony and arsenic gold deposit in central and western Hunan, the Sb and S weight percentage values of stibnite are stable at 0.72 and 0.28, excluding The gold stibnite changes greatly.

The gold element content in antimony ore is generally $0.14 \times 10-6 \sim 1.3 \times 10-6$, and part of it can be comprehensively utilized (Au>0.5×10-6). It is affected by the physical and chemical conditions and mineralization conditions during the formation of antimony (gold) deposits. In general, it is difficult to form an independent deposit of symbiotic antimony and gold due to the influence of mineralization. The gold and antimony elements in the deposit are mostly produced in association with each other.

The range of trace element content of stibnite in finely disseminated (Carlin type) gold deposits is relatively small, and the arsenic content is 0.165-4.79, which is significantly higher than the arsenic content of stibnite in antimony deposits;

the gold and silver contents are significantly higher (Ag is $1.04 \times 10-6 \sim 600 \times 10-6$, and Au is $0.75 \times 10-6 \sim 2900 \times 10-6$), which may be related to the mechanical mixing of more gold elements during the formation of antimonite.

The gold content in low-temperature gold-bearing antimony ore varies from $2.3 \times 10-6$ to $58.2 \times 10-6$, with an average value of $21.6 \times 10-6$. Its gold content is compared with that of pyrite, arsenopyrite, and arsenopyrite produced from antimony-gold deposits. Sulfides produced at slightly higher temperatures, such as chalcopyrite, have relatively low gold content. During the geological process, when the temperature of the hydrothermal fluid is high, the gold element is mostly in an ionic state dispersed in other symbiotic sulfides or adsorbed in the colloids of other minerals; when the temperature is low, the gold element in the hydrothermal fluid can naturally form gold. The form is directly precipitated. Stibnite forms at a lower temperature than most other sulfides (pyrite, arsenopyrite, chalcopyrite, etc.), which may be the main reason for its relatively low gold content. The low-temperature symbiotic mineral combination of stibnite and gold is very common in most hydrothermal gold deposits, and gold is mostly produced in the form of submicroscopic gold from stibnite.

By comparing the trace element characteristics of multiple antimony-gold deposits, the low-temperature gold-bearing antimony ore as a whole has a higher trace element content. The Co/Ni element content ratio characteristics of antimony and other gold-containing sulfides (such as pyrite, arsenopyrite, etc.) are highly similar, and the ratio decreases as the formation temperature decreases. The ratio of stibnite formed under medium temperature conditions is greater than 1, and the ratio of gold-bearing antimony formed under low temperature conditions is much less than 1.

3. GOLD CONTENT OF STIBNITE

The mineral (element) combinations in hydrothermal gold deposits vary greatly, and the gold content of stibnite also varies greatly. Its gold content has a certain relationship with the mineral generation period, mineral particle size, crystal form, chemical composition, production location in the deposit, and later alteration, etc. If the stibnite is produced in the Sb-Au metallogenic period, the mineral forms earlier, has a finer particle size (particle size $0.01 \sim$ 0.05mm), poor crystalline form, and is in the form of other-shaped granular, semi-hedral microgranular, and fine Produced as vein-like or massive aggregates, the gold content in the mineral is often higher; if it is antimonite in the Sb-Au symbiotic separation mineralization period, the mineral can often vary in size (0.05 \sim 2mm), and the degree of crystallization of the mineral single crystal Better, mostly euhedral, produced in the form of needle-shaped, radial, plate -shaped and other aggregates, but its gold content is often low. When Bao Zhenxiang studied the unique mineralization of antimony-gold deposits, he supported this feature from the aspects of element content, mineral metasomatic relationships, and submicroscopic gold production characteristics. It shows that the mineralization stage in which stibnite is formed is generally after the pyrite (arsenopyrite)-natural gold-quartz stage. Therefore, the earlier the stibnite is formed, the easier it is to obtain it during the geological process (encapsulation, adsorption, metasomatism). The gold element in the hydrothermal fluid increases the gold content of its minerals. In addition, Ai Guodong et al. found that the gold content of stibnite is also related to the impurity elements such as arsenic, tellurium, and selenium contained in the mineral itself. Those with higher impurity element content also have higher gold content, while those with purer chemical composition Stibnite contains Au and has very poor Au properties[9].

4. FORMATION PROCESS OF STIBNITE IN HYDROTHERMAL GOLD DEPOSITS

The crystallization process of antimonite is mainly restricted by temperature and reduced sulfur content; Krupp research showed that at 25°C and 90°C, the antimony element forms in the fluid as thioantimonite (Sb2S42-, HSb2S4 - and H2Sb2S40); at 200°C, the antimony element mainly exists in the form of Sb2S2(OH)2, followed by thiantimonite; when the hydrothermal temperature is 275°C and 350°C, Sb2S2(OH)2 As the main existing form of antimony element in the liquid, it is not affected by the pH value of the environment. Krupp and Williams-Jones et al. found that when the content of sulfur in hydrothermal fluids is particularly low, antimony will exist in the hydrothermal fluids in the form of antimony hydroxide (Sb(OH)3), Sb2S2 (OH)2 and Sb(OH)3 are the main substances that form antimonyite. The reaction chemical equation is: Sb2S2(OH)2+H2S=Sb2S3+2H2O; 2Sb(OH)3+3H2S=Sb2S3+6H2O[9].

This shows that the formation process of stibnite can only be carried out in a medium-low temperature reducing environment. When Zhang Zhenru et al. studied submicroscopic gold and lattice gold in minerals, they found that the submicroscopic gold in stibnite has similar production characteristics to the submicroscopic gold in pyrite, in the shape of small spheres and chains. It is in the shape of inclusions or cut by (010) cleavage of stibnite, indicating that the formation time of natural gold is earlier than that of stibnite. This conclusion is also confirmed by the inclusion temperature measurement results: the burst temperature of natural gold is 224° C, and the burst temperature of stibnite is 197° C[10].

Hydrothermal gold deposits with stibnite production mostly have a pyrite-arsenopyrite-quartz stage (I) in the deposit formation process. A large amount of arsenopyrite and pyrite are formed in the surrounding rocks accompanied by strong silicification; Au- As-Sb mineralization stage (II), forming natural gold-stibnite-natural antimony-natural arsenic -(gold, silver, copper, antimony, lead, zinc, iron and other sulfide and sulfate salt combination minerals)-quartz; late stage Sb mineralization stage (III), forming stibnite and natural antimony that are symbiotic with granular calcite; calcite stage (IV), forming calcite (-quartz) veinlets that cut through the ore body and surrounding rocks.

5 CONCLUSION

The study of the mineralogical characteristics of stibnite is of great value in both the theoretical study of hydrothermal gold deposits and the actual geological exploration process. With more and more in-depth research on hydrothermal gold deposits, research on different subdivided types of gold deposits still requires a comprehensive analysis of the geological background, ore-controlling factors, and mineralization conditions to understand the formation process of the deposits, and then Conduct detailed research on the physical and chemical characteristics of minerals such as pyrite, arsenopyrite, stibnite, chalcopyrite and other minerals, enrich and improve the physical and chemical conditions of mineral deposits, and mineral precipitation mechanisms from multiple perspectives, and ultimately form a practical prospecting and exploration model.

COMPETING INTERESTS

The authors have no relevant financial or non-financial interests to disclose.

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