ArcheoSciences
Revue d'archéométrie

33 | 2009
Authentication and analysis of goldwork

X-ray Diffraction method for determination of crystallite sizes of gold and silver items – New opportunities for archaeology and for protection against forgery

Méthode de diffraction de rayons X pour la détermination des tailles de cristallites des objets d'or et d'argent – Nouvelles opportunités pour l'archéologie et pour la protection contre la production de faux

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OpenEdition Journals

Electronic version
URL: http://journals.openedition.org/archeosciences/1985
DOI: 10.4000/archeosciences.1985
ISBN: 978-2-7535-1598-7
ISSN: 2104-3728

Publisher
Presses universitaires de Rennes

Printed version
Date of publication: 31 December 2009
Number of pages: 45-50
ISBN: 978-2-7535-1181-1
ISSN: 1960-1360

Electronic reference
Denka Yanakieva, Milena Tonkova, Ernst Spiridonov, Zlatil Vergilov and Petia Penkova, « X-ray Diffraction method for determination of crystallite sizes of gold and silver items – New opportunities for archaeology and for protection against forgery », *ArcheoSciences* [Online], 33 | 2009, Online since 09 December 2012, connection on 19 April 2019. URL : http://journals.openedition.org/archeosciences/1985 ; DOI : 10.4000/archeosciences.1985

Modern mineralogy of gold: overview and new data

Minéralogie moderne de l'or : bilan et nouvelles données

Ernst Spiridonov* and Denka Yanakieva**

Abstract: We suppose that it should be useful for archaeologists to have an overview on gold mineralogy, because 1) in ancient times, part of the golden objects were made directly from natural golden nuggets; 2) most of the Au in ores exists as its own minerals. The major part of the Au in the planets and meteorites of our Solar system is found in high temperature solid solutions: metallic Fe-Ni and monosulfides Fe-Ni and Fe-Cu. Au leaves them under fluid or some other reworking. As a result, Au minerals are formed. They are mainly developed in hydrothermal deposits of the upper part of Earth's continental crust. Au is the noblest chemical element. Thus, the most part of Au in deposits appears as native gold: Au-Ag, Au-Ag-Hg, Au-Cu, Au-Pd, and Au-Pt system minerals. The most important feature of native gold is its fineness, i.e. the Au content in the mineral species, expressed in ‰. Chalcogenides of Au – sulfides and selenides, and, similar to them, tellurides, plumbotellurides, antimonides, bismuthides – are not so widespread. Data on the 44 Au mineral species known today are provided in this overview. The first quantitative estimations of natural native gold nano-dimensional crystallites of several mesothermal deposits are enclosed.

Résumé : *Nous supposons qu'il est important pour les archéologues d'avoir une vue générale sur la minéralogie de l'or car : 1) dans le passé une partie des objets en or ont été produits directement à partir de pépites d'or ; 2) la plus grande partie de l'or existe sous la forme de ses propres minerais. La plus grande partie de l'or dans les planètes et les météorites de notre système solaire se trouve en solutions solides à haute température : Fe-Ni métallique et Fe-Ni monosulfites et Fe-Cu. L'or les laisse sous la forme de fluides ou sous une forme équivalente. Le résultat est la formation de minerais d'or. Ces minerais sont essentiellement développés dans des gisements hydrothermaux de la partie supérieure de la croûte terrestre. L'or est l'élément chimique le plus noble. Pour cette raison, la majorité de l'or dans les gisements se présente sous forme native : systèmes minéraux Au-Ag, Au-Ag-Hg, Au-Cu, Au-Pd, Au-Pt. La caractéristique la plus importante de l'or est son titre, c'est-à-dire la quantité d'or dans les espèces minérales en ‰. Chalcogenides d'or – sulfites et sélénites et similaires comme les tellurites, plumbotellurites, antimonides, bismuthides – sont moins répendus. Les données des espèces minérales ^{44}Au connues actuellement sont fournies dans cet article. Les premières estimations quantitatives de cristallites nano-dimensionnelles d'or natif naturel de divers gisements mesothermiques ont aussi été inclues.*

Keywords: mineralogy, gold, nanomineralogy.

Mots-clés : *minéralogie, or, nano-minéralogie*

1. Introduction

The major part of the Au in the planets and meteorites of our Solar system is found in high temperature solid solutions – metallic Fe-Ni and monosulfides Fe-Ni (Mss) and Fe-Cu (Iss). Au leaves them under fluid reworking. As a result, Au minerals are formed. They are mainly developed in hydrothermal deposits of the upper part of Earth's continental Earth. Au is the noblest chemical element. Thus, the most part of Au in deposits appears as native gold – Au-Ag, Au-Ag-Hg, Au-Cu, Au-Pd, and Au-Pt system minerals. The most important feature of native gold feature is its fineness, i.e. the Au content in the mineral specimen, expressed in ‰. Chalcogenides of Au – sulfides and selenides, and, similar to them, tellurides, plumbotellurides,

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rec. Sept. 2009 ; acc. Nov. 2009

antimonides, bismuthides – are not so widespread. Much Au is found as the finest impurity in hydrothermal nonstoichiometric As-bearing pyrite $Fe(S,_{As})_{2-x}$ and arsenopyrite $FeAs_{1-y}S_{1+y}$ and bitumen-like Au-organic compounds.

2. Au – Ag system minerals

The main part of native gold appears as cubic solid solutions – Au-Ag system minerals. According to the results of thousands of precision analyses (Brauns, 1906; Vernadsky, 1914; Lindgreen, 1933; Smolin, 1970; Editorial Committee, 1970; Petrovskaya, 1973; Berman *et al.*, 1978; Nedra, 1984-1990; Oberthür and Saager, 1986; Shikazono and Shimizu, 1987; Amuzinsky *et al.*, 1992; Nekrasov *et al.*, 1994; Spiridonov, 1995; So *et al.*, 1995; Frimmel and Gartz, 1997; Hytőnen, 1999; Knight and Leitch, 2001, etc.) it was established that the series Au-Ag is uninterrupted in composition. These series are fixed in the limits of the series (Vernadsky, 1914; Petrovskaya, 1973): **gold** (0-30 wt% Ag; fineness 1000-700); **electrum** (30-70 wt% Ag; fineness 700-300); **kuestelite** (70-90 wt% Ag; fineness 300-100); gold-containing **silver** (90-100 wt% Ag; fineness 100-0). The confirmed mineral species are noted in bold. On observations of the authors, the phenomena of disintegration of solid solution in Au-Ag minerals are not shown. The size of gold crystals varies from colloidal (< 0.1 microns) up to several cm, usually around a fraction of mm. Colloidal gold colours a chalcedony-like quartz in green colour (Baley, Transbaykalia). The size of the granulated intergrowths of gold (nuggets) is up to one metre. As Al-Biruni (1963) noted, the largest nugget of gold discovered weighed ~ 2500 kg (Zaruban, Afganistan).

High-standard gold (Fig. 1) is typical for plutonogenic hydrothermal gold-quartz deposits. These formations are the main source for placer Au deposits. Electrum, kuestelite and Au-bearing silver, their dendrites, skeletal and wire-shaped crystals (Fig. 2) are typical for volcanogenic hydrothermal Au-Ag deposits (Goldschmidt, 1918; Lindgreen, 1933; Petrovskaya, 1973). Widespread in these deposits, electrum corresponds to the famous 'electron' of the ancient Greeks, and the favourite 'white gold' of the Incas.

Gold crystals of primary endogenic deposits are zonal: later zones are enriched by Ag and Hg (usually insignificantly). In metamorphosed deposits, grains of gold are azonal, and intergrowths of different composition are observed (Frimmel and Gartz, 1997). In placers, grains of gold are usually enclosed by margins of porous high-standard gold; silver from these margins is leached. In placers, native gold often is found together with minerals of platinum group elements (ferroplatinum Pt_3Fe, alloys Os-Ir-Ru, etc.).

Figure 1: (See colour plate) Gold (fineness 885) in quartz vein. 81 mm. Bestube, Northern Kazakhstan. Collection and photography – E.S. Perhaps this deposit was one of the gold sources for the well known ancient Scythian jewellery.

Figure 1 : (Voir planche couleur) Or (titre 885) dans le filon de quartz. Bestube, nord du Kazakistan. Collection et photographie – E.S. Peut-être ce gisement a été une source d'or, exploité pour la production d'orfèvrerie Scythe.

3. Au (Ag) – Hg system minerals

After Ag, Hg is the second most typical element impurity in native gold. In ores formed under low f S_2 conditions, there are cubic α-amalgams: **mercurian gold (Au, Hg)** (Nazmova and Spiridonov, 1979; Oberthür and Saager, 1986; Shikazono and Shimizu, 1988; Amuzinsky *et al.*, 1992); **mercurian electrum (Au, Ag, Hg), mercurian kuestelite (Ag, Au, Hg),** gold-containing **mercurian silver** (Spiridonov and Pletnev, 2002). Mercurian gold contains up to 18 wt% Hg, and mercurian silver up to 26% Hg. Au amalgams enriched by Hg are much more rare. They usually associate with native Hg: hexagonal **weishanite** $\mathbf{(Au,Ag)_3Hg_2}$ (Li *et al.*, 1984; Wu, 1993); cubic **gold amalgama** $\boldsymbol{\gamma}$**-**$\mathbf{Au_2Hg_3}$ (Berman and Harcourt, 1938). Almost all Au amalgams found in placer deposits are technogenic formations (Wu, 1993).

4. Au – Cu system minerals

Cu is the third most typical element impurity in native gold, after Ag and Hg. Au-Cu phases poor in silver and Au-Ag phases poor in copper are formed at temperatures below 350 °C (Lyakischev, 1996). Au-Cu minerals (cuprian

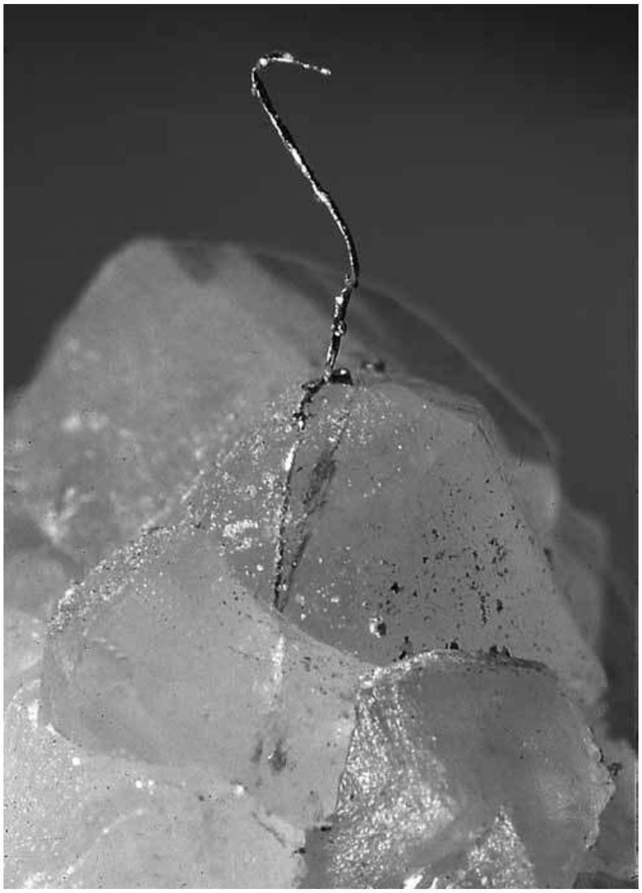

Figure 2: (See colour plate) Golden wire in calcite. 4 mm. Tyrny-Auz, Northern Caucasus. Collection of V. Andreenko. Photography – M. Bogomolov.
Figure 2 : (Voir planche couleur) Fil d'or dans de la calcite. 4 mm. Tyrny-Auz, nord du Caucase. Collection de V. Andreenko. Photographie M. Bogomolov.

gold) are found in hydrothermal Au deposits, among listvenitized peridotites, komatiites and rodingites (Lozechkin, 1939; Spiridonov and Pletnev, 2002). These last minerals replace native copper. Cubic **auricupride $AuCu_3$** is known (Ramdohr, 1967). Metastable **cuproauride AuCu** corresponds to the low ordered α-(Au, Cu) solid solution (Lozechkin, 1939; Chvileva *et al.*, 1988). The mineral corresponding to the Au_3Cu cubic modification (Knipe and Fleet, 1997; Spiridonov and Pletnev, 2002) does not have an authorized name. Below, it is referred to as **mineral Au_3Cu**. The products of cuproauride solid phase transformation are tetragonal **tetraauricupride AuCu** (Chen *et al.*, 1982). Tetraauricupride can contain up to 17 wt% Pd (Spiridonov *et al.*, 2003). Tetraauricupride – hongshiite CuPt solid solutions are known (Kwitko *et al.*, 2002). After annealing, non-stoichiometric cuproauride $Au_{1+x}Cu$ shows two types of thin lattice solid solution disintegration structures: Au + tetraauricupride and tetraauricupride + mineral Au_3Cu. The disintegration structures are known, where the matrix is Au and lamellas are mineral Au_3Cu; probably they are products of the non-stoichiometric mineral $Au_{3+x}Cu$'s disintegration. The standard roentgenometric data that are required for the determination of Au-Cu system minerals are provided in Chvileva *et al.* (1988).

5. Au – Fe system minerals

It was established by a combination of magnetometric and mineralogical methods that the high-magnetic ferrous gold with 4-5 wt% Fe described earlier shows fine crystal intergrowths of gold with 0-0.2 wt% Fe, and magnetite octahedrons 0.01-0.2 microns in size (Yacubovskaya *et al.*, 1989).

6. Au – Pd, Pt, Os, Ir system minerals

Au-Pd and Au-Pt system minerals are typical rare minerals of telethermal Au deposits formed at low f S_2 and at heightened f O_2. They are cubic **palladian gold (porpezite) (Au, Pd)**. (Vernadsky 1914; Kwitko *et al.*, 2002)**; platinian gold (Au, Pt)** (Levin *et al.*, 1986); intermetallides with compositions similar to Pt_3Au and Pt(Au,Pd). Even a low impurity of Pd (of the order of a few percent) results in the steel-grey colour of this type of native gold.

7. Au – Bi, Sb, Pb, Sn system minerals

Intermetallides of gold – **maldonite Au_2Bi** (Hytőnen, 1999) and **aurostibite $AuSb_2$** (Graham and Caiman, 1952; Spiridonov, 1995) are rather rare minerals of hydrothermal ores. Maldonite contains ~ 65 wt% Au, and aurostibite ~ 45 wt% Au. Aurostibite pseudomorphs after maldonite are rarely encountered; such aurostibite contains up to 9 wt% Bi. These minerals are formed under low f S_2. Maldonite usually replaces native bismuth. Aurostibite usually replaces native gold. The following three intermetallides: **anyuiite $AuPb_2$** (Razin and Sidorenko, 1989), **hunchunite Au_2Pb** (Shangquan *et al.*, 1992), **yuanjiangite AuSn** (Chen Lichang, 1994) are found only in placers. Perhaps these three intermetallides are technogenic products.

8. Au – Ag (Cu) – Te system minerals

Au and Ag tellurides are typical minerals of hydrothermal Au deposits. In a series of cases, they are the main Au and Ag bearing minerals in ores. Hg and Cu are typical elemental impurities in these tellurides. Triclinic **montbrayite $Au_2(Te,_{Sb,Pb,Bi})_3$** (Peacock and Thompson, 1946; Chvileva *et al.*, 1988) is a rare telluride, and it contains ~ 50 wt% Au and up to 5 wt% Sb. Monoclinic **calaverite $AuTe_2$** (Stillwell, 1931; Markham, 1960) contains ~ 45 wt% Au, and usually < 0.5 wt% Ag. In some deposits (Kalgoorly, Australia), there are calaverite aggregates reaching $1m^3$ in size. Rhombic **krennerite $Au_3(Au,Ag,Cu)Te_8$** (Markham, 1960; Editorial Committee, 1970; Chvileva *et al.*, 1988) contains ~ 40 wt% Au, and 0.5-6.5 wt% Ag; its composition varies from $AuTe_2$ to Au_3AgTe_8. Monoclinic **silvanite $Au(Ag,Au,Cu)Te_4$** (Stillwell, 1931; Markham, 1960; Editorial Committee 1970; Chvileva *et al.*, 1988) contains ~ 25 wt% Au. **Kostovite $Au(Cu,Ag,Au)Te_4$** (Terziev, 1966), similar to silvanite, is a typical reactionary mineral of volcanogenic Au ores. **Mutmannite $AuAgTe_2$** (Spiridonov and Chvileva, 1985), developed in the cementation zone of the gold-telluride deposits, is an example of mimicry in the mineral kingdom, because it is indistinguishable from petzite optically and on spectra of reflection light, and from calaverite according to the X-ray pattern. Cubic **petzite $AuAg_3Te_2$** (Markham, 1960; Chvileva *et al.*, 1988) with garnet-like structure is the most widespread Au-Ag telluride; it contains ~ 25 wt% Au. Cubic **solid solution $(Ag,Au)_2Te$** is rarely encountered as homogeneous phase; usually it is transformed into petzite and hessite intergrowths.

9. Au – Ag – Se, S system minerals

Cubic **fischesserite $AuAg_3Se_2$** (Johan *et al.*, 1971), cubic **uytenbogaardtite $AuAg_3S_2$** (Barton *et al.*, 1978), monoclinic **petrovskaite AuAgS - AuAg(S,Se)** (Nesterenko *et al.*, 1984; Nekrasov *et al.*, 1988), hexagonal **penzhinite $AuAg_4(S,Se)_4$** (Bochek *et al.*, 1984), cubic **solid solution $(Ag,Au)_2Se$** (Spiridonov *et al.*, 2009), cubic **solid solution $(Ag,Au)_2S$** (Samusikov *et al.*, 2002) are typical minerals of Au volcanogenic hydrothermal deposits, from low sulfide to rich sulfide ones. Petrovskaite is also developed in crusts of weathering of sulfide rich deposits, in association with jarosite and native sulphur.

10. Complex chalcogenides

Rhombic **nagyágite $AuPb_5Te_{4-x}(Sb,As)_xS_6$** (Spiridonov, 1991a; Simon *et al.*, 1994) – **$AuPb_5Te_2(Sb,Bi)S_6$** (Johan *et al.*, 1994), monoclinic **museumite $AuPb_5SbTe_2S_{12}$** (Bindi and Cipriani, 2004), rhombic **buckhornite $AuPb_2BiTe_2S_3$** (Francis *et al.*, 1992; Johan *et al.*, 1994), monoclinic **criddleite $Au_3Ag_2TlSb_{10}S_{10}$** (Harris *et al.*, 1988), monoclinic **jonassonite $AuBi_5S_4$** (Paar *et al.*, 2006) are typical formations of Au and Au-Ag volcanogenic hydrothermal deposits. Nagyágite – 'grey foliated gold ore' – is the most widespread among them.

11. Plumbotellurides and stibio-plumbo-tellurides of the Au-Cu-Fe system

These hypergenic minerals are developed in the cementation zone of gold-telluride deposits. They are monoclinic (?) **bilibinskite $Au_5Cu_3(Te,Pb,)_5$** and **bilibinskite-(Sb) $Au_6Cu_2(Te,Pb,Sb)_5$** (Spiridonov, 1991b), rhombic (?) **bogdanovite-(Cu) – $Au_5Cu_3(Te,Pb)_2$** and **bogdanovite-(Fe) – $Au_5CuFe_2(Te,Pb)_2$** (Spiridonov, 2008), monoclinic (?) **bezsmertnovite $Au_4Cu(Te,Pb)$** (Spiridonov, 1991b). Bilibinskite, bogdanovite and bezsmertnovite contain ~

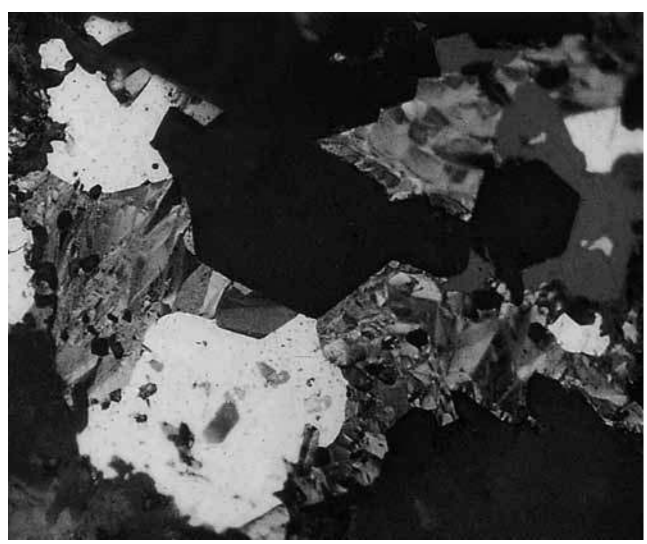

Figure 3: (See colour plate) Bogdanovite (pseudomorph after kostovite) in gold-quartz vein. 2 mm. Bogdanovite with strong coloured bireflection. Polished section in reflected light. Aginskoe, Kamchatka. Collection and photography – E.S.
Figure 3 : (Voir planche couleur) Bogdanovite (pseudomorphe de kostovite) dans le filon de quartz aurifère. Bogdanovite avec biréflectione fortement colorée. Section polie sous lumière réfléchie. Aginskoe, Kamchatka. Collection et photographie – E.S.

50, 65 and 75 wt% Au, respectively. Macroscopically, they have the appearance of bornite. In reflected light, they are very specific, being characterized by bright colour double-reflection (Fig. 3) and anisotropy. Bilibinskite, bogdanovite and bezsmertnovite replace kostovite, krennerite, silvanite, and nagyágite. In the oxidation zone, plumbotellurides of gold are substituted by finely scalloped gold and tellurides of Cu, Pb, and Fe.

12. Conclusion

Brief data on the 44 gold mineral species known today are provided above. Each of them has an individual chemical composition, crystal structure, X-ray pattern, unit cell parameters, physical properties (colour, hardness, spectra of reflection light, etc.). For many of these minerals, the most important feature is their fineness, i.e. Au content expressed in ‰.

A main new feature – new characteristic of gold minerals – could probably be related to the area sizes of X-radiation coherent dissipation, i.e. the crystallite size. For the majority of crystal matters, the crystallites' size is nano-dimensional, ranging from a few nm up to several hundreds of nm. The description of the crystallites size can be found in a paper by D. Yanakieva and co-authors in this issue of *ArcheoSciences*. The first interesting data on the nano-dimensions of crystallites is obtained. High-standard gold from large mesothermal deposits in Northern Kazakhstan, with an age of 445 ± 4 Ma, is studied. These deposits are of a different depth facies – hypabyssal Au-Sb Bestube, mesoabyssal Au Stepnyak, abyssal Au-telluride (Spiridonov, 1995). One of the studied specimens from Bestube is shown in Figure 1. The crystallite sizes of tens of studied Bestube gold specimens are 20.0 ± 0.2 nm; for Stepnyak gold, 21.6-21.8 nm; for Aksu gold, 26.0 ± 0.3 nm (investigator D. Yanakieva). Thus, for this group of deposits, the direct correlation between the size of crystallites and the depth of formed gold ores is established. The size of the crystallites of hypergenic gold from Zana-Tube is quite different: 31.3-31.8 nm.

Acknowledgements

This research was supported by grant no. 07-05-00057 of the Russian Foundation for Basic Research.

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