

HYDROTHERMAL SYNTHESIS OF GOLD, ELECTRUM AND ARGENTITE

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ABSTRACT

The dissolution and precipitation of gold and silver at 150°C were investigated in various strongly acid solutions and aqueous NaHS, over periods of 60 and 120 days. Starting material was a synthetic Au₅₀Ag₅₀ alloy. Millimeter-sized free-growing euhedral crystals of pure gold were obtained only from 6N HCl solution after 120 days; no precipitation of either gold or silver was obtained from the sulfuric and nitric acid solutions. The gold crystals appear to be flattened cuboctahedra and are very similar to electrum crystals from Japanese epithermal gold deposits. Small crystals of both electrum (Au₇₁Ag₂₉) and argentite were precipitated onto the starting alloy sample after 120 days in 5.2 m aqueous NaHS. The sulfur fugacity of the experimental solution is estimated to have been 10^{-11.8} atmospheres, at a pH of 12.98.

Keywords: hydrothermal synthesis, gold, electrum, argentite.

SOMMAIRE

Nous avons étudié la dissolution et la précipitation de l'or et de l'argent à 150°C dans des solutions fortement acides et dans une solution aqueuse de NaHS, sur une période de 60 à 120 jours. Le matériau de départ était un alliage synthétique de composition Au₅₀Ag₅₀. Nous avons obtenu des cristaux millimétriques idiomorphes d'or pur après 120 jours dans une solution de 6N HCl. Aucune précipitation d'or ou d'argent n'a lieu à partir de solutions des acides sulfurique et nitrique. Les cristaux, cuboctaèdres aplatis, ressemblent beaucoup aux cristaux d'électrum des gisements japonais d'or épithermaux. De petits cristaux d'électrum (Au₇₁Ag₂₉) et d'argent sont précipités sur la surface de l'alliage de départ après 120 jours dans une solution aqueuse de 5.2 m NaHS. La fugacité du soufre dans cette solution aurait été de 10^{-11.8} atmosphères, et le pH, 12.98.

(Traduit par la Rédaction)

Mots-clés: or, argent, électrum, synthèse hydrothermale.

INTRODUCTION

Investigations on the solubility of gold in HCl aqueous solution and others have been reported by Ogryzlo (1935), Henley (1973), Glyuk & Khlebnikova (1980) and Shikazono *et al.* (1990). Electrum (Au-Ag alloy) was synthesized by Shilo *et al.* (1974) using an electrochemical method and at room temperature and pressure by Honma & Nakata (1986) in the system gold - sodium sulfite - silver nitrate - activated carbon - water. The present study is a continuation of that work, in which the hydrothermal dissolution and precipitation of gold and silver from a synthetic alloy starting material of composition Au₅₀Ag₅₀ (molar proportions) was investigated. The solutions used were either strong acids or aqueous NaHS (5.2 m) at 150°C, for periods of either 60 or 120 days. Large euhedral gold crystals (Au₁₀₀Ag₀) were obtained only from 6N HCl solution after 120 days. The 120-day experiment in the presence of a NaHS solution produced both electrum (Au₇₁Ag₂₉) and argentite as small crystals growing on the starting-alloy sample. To our knowledge, this is the first report of either the hydrothermal synthesis of millimeter-scale gold crystals or the simultaneous deposition of electrum and argentite from sulfide media.

EXPERIMENTAL

Acid systems

The acid solutions investigated were 36N and 18N H₂SO₄, 12N and 6N HNO₃ and 6N HCl. In each case, approximately 60 mL of the acid solution was placed into a teflon reaction tube together with about 0.2 g of synthetic Au₅₀Ag₅₀ alloy. On the basis of electron-microprobe data, the alloy is compositionally homogeneous within ± 2 wt. % Au. The teflon

TABLE 1. Au AND Ag CONTENTS IN EACH SAMPLE SOLUTION AND WEIGHT OF EACH GRAIN AT START AND END OF EXPERIMENT

run number	Au (ppm)		Ag (ppm)		solution colour	precipitate*	weight of grain (g)	
	60d	120d	60d	120d			start	end
1	36N H ₂ SO ₄	0.0		5.50	pale yellow	X	0.2398	0.2387
2	18N H ₂ SO ₄	1.48		0.69	pale yellow	X	0.2188	0.2187
3	12N HNO ₃	0.13		0.0	colourless	X	0.2042	0.2041
4	6N HNO ₃	0.39		0.54	colourless	X	0.2156	0.2150
5	6N HCl	0.28		53.8	colourless	X	0.1983	0.1951
6	6N HCl	103.2		1538	pale yellow	+	0.2186	0.0943

* + and X mean that precipitates exist or not, respectively.

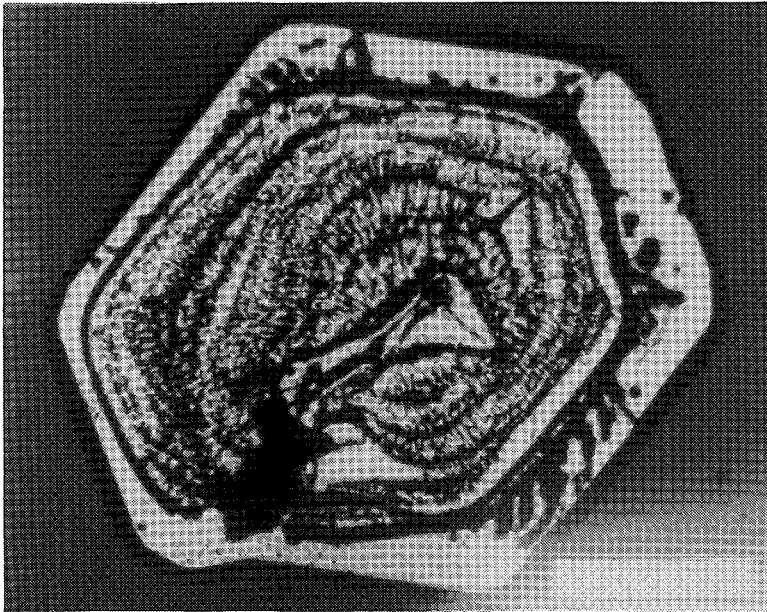


FIG. 1. A large euhedral crystal of Au₁₀₀Ag₅₀ in experiment number 6. Bar is 1 mm.

tubes used in these runs had a length of 25 cm, an external diameter of 3 cm, and a wall thickness of 0.5 cm. The tube was sealed in air, enclosed in a stainless steel casing, and placed in an electric furnace, the temperature of which was controlled at $150 \pm 3^\circ\text{C}$ for periods of either 60 or 120 days. At the end of the runs, the tubes were air-cooled to room temperature, and the reaction products decanted and examined for the presence of precipitated material and solution color. Quantitative determinations of solution compositions (Table 1) were obtained by atomic absorption spectrometry (Seiko model SAS-760).

NaHS solution

The same Au₅₀Ag₅₀ alloy material and experimental procedure that was used in the acidic experiments also formed the basis of the run in an alkaline medium. A sample of the alloy weighing 779.5 mg was placed in a teflon tube with 125 mL of 5.2 m NaHS aqueous solution (pH 12.38) and maintained at $150 \pm 3^\circ\text{C}$ for 120 days. At the end of the run, the tube was opened and found to contain only a modified form of the original sample, weighing 755.1 mg, in a solution (pH 12.98) assaying 154.0 ppm Au and 9.8 ppm Ag.

DISCUSSION

Acid systems

Somewhat surprisingly, no precipitation or change in the color of the solution and only minimal dissolution of both gold and silver were observed (Table I) in the nitric acid solutions. In sulfuric acid there was enhanced, but still minimal, dissolution of both gold and silver, the solution color changed to pale yellow, but there was no precipitation. Precipitation of gold was obtained only from the 6N HCl solution after 120 days of reaction (run #6, Table I). The 60-day 6N HCl sample showed considerable dissolved silver, but only traces of dissolved gold, which roughly fitted an extrapolation of the gold solubility data of Glyuk & Khlebnikova (1980); however, the solution was colorless, and there was no precipitate formed.

The precipitate obtained from experiment number six consisted of euhedral crystals of brilliant shiny metallic gold (Fig. 1) (about 20 mg), together with a large number of small elongate crystals (0.05 to 0.4 mm) of silver chloride (cerargyrite, about 50 mg). The three largest crystals of gold ranged in size from one to four mm (about 3 to 5 mg), and no silver could be detected by electron-microprobe analysis. These gold crystals are very similar morphologically

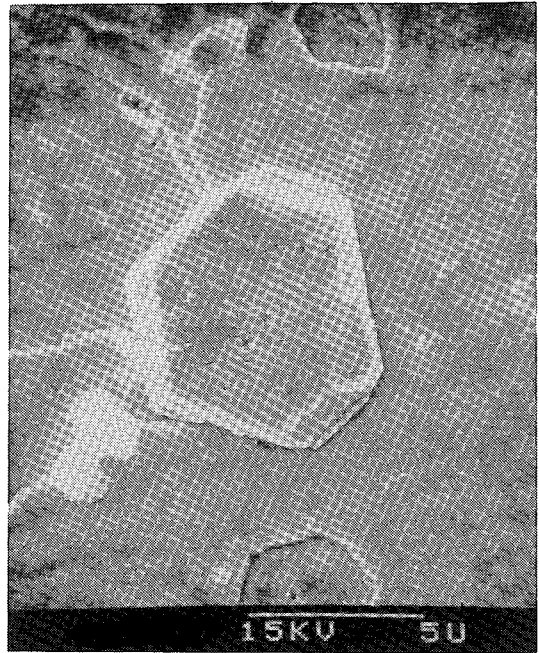


FIG. 2. A euhedral crystal of electrum from the Seigoshi epithermal gold vein-type deposits, Shizuoka Prefecture, Japan.

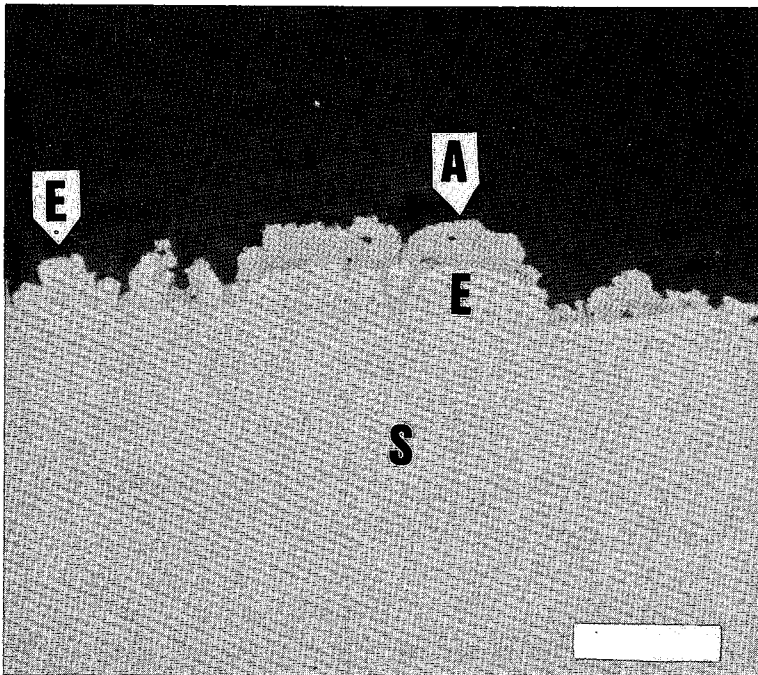


FIG. 3. Photomicrograph of a polished section of the post-reaction sample. S: $\text{Au}_{50}\text{Ag}_{50}$ alloy, E: electrum, A: argentite. Bar is 50 μm .

TABLE 2. CHEMICAL COMPOSITION (ELECTRON-MICROPROBE DATA) OF COEXISTING ELECTRUM (E) AND ARGENTITE (A) PRECIPITATED DURING THE EXPERIMENT

	weight percent				atomic percent		
	Au	Ag	S	Total	Au	Ag	S
E	81.76	18.04	-	99.80	71.31	28.69	-
A	-	87.03	12.99	100.02	-	66.57	33.43

Instrumentation: JEOL electron microprobe at the Ocean Research Institute, University of Tokyo, run at 25kV. Standards: pure elements (for Au) and synthetic Ag_3HS_3 (Ag).
Lines: AuL α and AgL α .

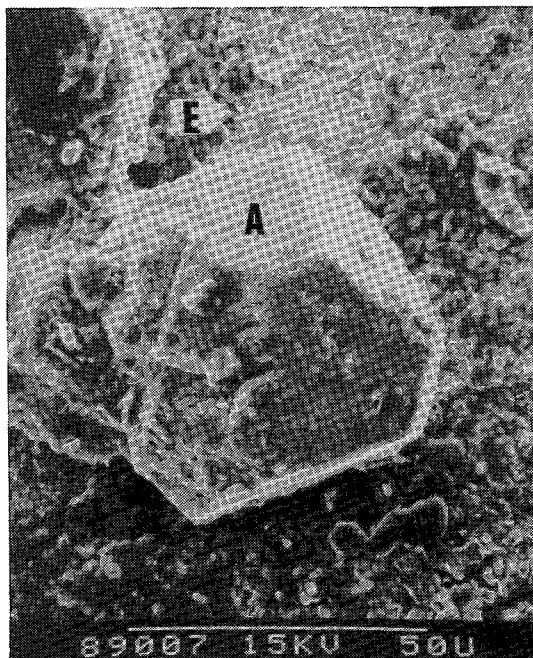


FIG. 4. SEM photomicrograph of the surface of the post-reaction sample. E: electrum, A: argentite.

to crystalline specimens of electrum ($\text{Au}_{47}\text{Ag}_{53}$; Shikazono 1978) from the Seigoshi epithermal gold vein deposits (Fig. 2), Izu Peninsula, Shizuoka Prefecture.

NaHS solution

The post-reaction sample from this experiment showed clear evidence of substantial change from the original alloy material. Portions of the surface were a greyish color, and both individual and aggregates of isometric crystals were visible. In polished section (Fig. 3), a surface growth of small gold crystals (highly flattened octahedra?) and rounded bumps were somewhat more golden in color than the bulk of the alloy. Electron-microprobe analysis of the phases (Table 2) showed them to be very homogene-

ous, and the newly deposited electrum to be considerably richer in gold ($\text{Au}_{71}\text{Ag}_{29}$) than the parent alloy ($\text{Au}_{50}\text{Ag}_{50}$). The grey phase has both the composition and the X-ray-diffraction pattern of argentite; isolated crystals (Fig. 4) are euhedral cuboctahedra.

The assemblage electrum-argentite is common in hydrothermal gold deposits and can be used to estimate the fugacity of sulfur in the system (Barton & Toulmin 1964). Application of their method to the post-reaction electrum composition yields a value of $f(\text{S}_2)$ of $10^{-11.8}$ atmospheres for the experimental solution. This is in reasonable agreement with an extrapolation to pH 13 of the data of Seward (1973) for the gold complex $\text{Au}_2(\text{HS})_2\text{S}^{2-}$.

SUMMARY

In the systems $\text{Au}_{50}\text{Ag}_{50}$ alloy - various strongly acid solutions, only the 60-day and the 120-day 6N HCl samples showed considerable dissolved gold or silver (or both) at 150°C. In the 120-day 6N HCl sample only, millimeter-sized free-growing euhedral crystals (of cuboctahedral form) of pure gold were obtained with fine crystals of silver chloride.

In the system $\text{Au}_{50}\text{Ag}_{50}$ alloy - NaHS solution (5.2 m), electrum ($\text{Au}_{71}\text{Ag}_{29}$) and argentite were produced in or onto the starting alloy sample at 150°C after 120 days.

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