THE SOLUBILITY OF GOLD IN FERRIC SULPHATE AND ITS GEOLOGICAL APPLICATIONS.

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(Received Nov. 8, 1934).

ABSTRACT.

Gold was found to be slightly soluble in ferric sulphate solutions, and quite soluble in solutions of ferric sulphate with a small amount of sulphuric acid. It is possible to explain the phenomenon of supergene enrichment of gold deposits by means of this solubility of the gold in ferric sulphate, which is formed by the oxidation of pyrites, a common associate of gold.

The question of the solubility of gold in ferric sulphate is of interest in Geology because it offers an explanation for one of the problems of Geology, viz., that of secondary enrichment of gold deposits. In some gold deposits there is evidence to show that some of the gold was deposited as the result of secondary action. It appears that the gold was concentrated in a lower horizon by supergene solutions which carried gold obtained by the leaching of an upper portion of the same deposit. What is the solvent responsible for this action?

Ferric sulphate has several times been suggested as this solvent, because it is formed in most gold deposits by the oxidation of pyrites, a common associate of gold. In the older literature ferric salts were mentioned as solvents of gold, but later writers have denied this, stating that gold can only be dissolved by solutions capable of producing nascent chlorine. H. Wurtz¹ has stated that gold is soluble in ferric sulphate under proper conditions, while Stokes², W. H. Emmons ³, J. R. Don⁴, and others have said that ferric sulphate is in-

Proc. N. S. Inst. Sci., Vol. xviii, pt. 4.

¹ H. Wurtz, A. J. Sc., 1858, p. 51. Lindgren, "Mineral Deposits", 3rd. ed., p. 966.

² Stokes, Econ. Geology, 1906.

⁸ W. H. Emmons, Bull. 625, U. S. Geol. Survey.

⁴ J. R. Don, Trans. American Inst. of Mining and Engineering.

effective in dissolving gold. This work was undertaken for the purpose of determining the solubility of gold in ferric sulphate.

The solvent effect of ferric sulphate was tried in two ways, first by etching a polished surface of gold with the ferric sulphate, and secondly by placing gold in a solution of ferric sulphate and testing the solution for the presence of gold.

In the first method the solvent effect was shown by the way the polished surface was etched. In the second method the presence of gold in the solution was determined by means of a microchemical test, that described by Putnam, Roberts, and Selchow⁵. The reagent used was a 10% solution of pyridine in 40% hydrobromic acid. This solution, when added to a drop of the solution containing gold, gave a precipitate of fine feathery-like crystals, which, between the crossed nicols of the microscope, were bright yellow. The presence of the ferric sulphate gave a precipitate of larger red-colored crystals which could easily be distinguished from the crystals due to the gold. Blank tests were run on all the reagents so as to be sure that a positive result indicated without doubt the presence of gold in the solution.

First a rock specimen containing gold was polished and then placed in a solution of ferric sulphate. Due to the presence of carbonates in the rock it was necessary to add a small amount of sulphuric acid in order to keep the ferric sulphate in solution. In a solution at room temperature no sign of etching was visible at the end of fifteen minutes, but when the solution was warmed to about 70-80 °C. the surface of the gold was seen to be slightly etched, showing the solubility of gold in the solution used. Due to the presence of the sulphuric acid in the solution it could not be determined whether or not gold is soluble in pure ferric sulphate, but only that it is soluble in ferric sulphate solutions containing a small amount of sulphuric acid. However natural supergene solutions contain sulphuric acid.

⁵ Putnam, Roberts, and Selchow, "Contributions to Determinative Mineralogy."

In the second method gold foil was used. Small pieces were placed in various solutions and these solutions tested for gold.

The first solution of ferric sulphate after standing for half an hour did not give a definite test for gold, but on standing over night enough gold dissolved to give a satisfactory test showing the presence of gold.

Another solution was heated to about 70-80°C., and after fifteen minutes the test showed the presence of gold in the solution.

The next solution was boiled in order to hasten the action. After twenty minutes the presence of gold in the solution was shown by the microchemical test. This, however, has no application to the problem of supergene enrichments, since these solutions do not reach such a temperature.

Another solution was made up containing besides the ferric sulphate about one per cent. of sulphuric acid. This boiling solution completely dissolved quite a large piece of the gold foil, and upon cooling some of the gold was deposited as a film on the surface of the liquid.

These experiments show that gold is slightly soluble in cold solutions of ferric sulphate, and at higher temperatures the solvent action is greater. The presence of a small amount of sulphuric acid greatly increases the solubility of the gold.

A test for ferrous sulphate was negative, so it appears that the gold does not reduce the ferric sulphate.

In supergene enrichments of gold deposits it is supposed that the ferric sulphate and sulphuric acid is formed by the oxidation of iron pyrites as follows:

An example of this secondary enrichment is found in the gold deposits at the Rio Tinto Mine in Spain. The ore is pyrites carrying copper and a little gold. The deposit has been oxidized at the surface leaving a gozzan. Below this

gozzan is a thin layer of black to yellow muddy material, about twenty to thirty centimeters thick. This layer has a much higher gold content than the rock above or below. This is the result of secondary enrichment. The oxidation of the pyrites above formed ferric sulphate and sulphuric acid, which seeping downwards dissolved the gold in the ore, and when it reached the fresh pyrites the gold was precipitated. The analysis of these different layers is shown in the accompanying diagram.

PROPORTIONS OF GOLD AND SILVER AT VARIOUS DEPTHS AT RIO TINTO.

		-	Gold	Silver
1.	Gozzan	1. 2. 3.	5.2 33.6 23.2 6.4	2.68 83.43 50.69 25.48
2.	Black Earth	1. 2. 3. 4. 5. 6. 7. 8. 9.	6.4 7.2 6.0 3.2 4.0 2.6 3.6	20 .40
3.	Yellow Earth			
	:	Gold in a Silver in d	grams per 1,000 kild oz. per ton.	ograms.
		Figures th	rough courtesy of Pr	of. G. V. Douglas.
4. to 10.	Grey Earth			

This theory accounts for the gold in these layers. If ferric sulphate acting for only a short time in the laboratory can dissolve gold, then in the long time in which it could act in nature it could leach out the gold in the oxidized portion of an ore body and account for the lower enrichments.

The case of the Rio Tinto deposits has been described by Prof. G. V. Douglas⁶ and Prof. Davis Williams⁷, and similar cases have been reported by other writers from South Africa and South America. Ferric sulphate, with sulphuric acid, seems to be the general solvent in these cases, and due to its common occurrence it is probably the chief solvent responsible for supergene enrichments of gold deposits.

This work was done as part of a course in Geology at Dalhousie University under the direction of Professor G. V. Douglas. It is a pleasure to acknowledge the assistance of Prof. Douglas and also of Mr. C. W. McKinnon, who helped not only in the work but also in preparing the paper for publication.

⁶ G. V. Douglas, Geol. Mag., Vol. 66, p. 302.

⁷ D. Williams, Inst. of Mining and Metallurgy, April, 1934.