速報

Dissolution of Ir and Os in Hydrothermal 1N and 3N HCl Solutions at 150°C*

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Experiments on dissolution of Ir and Os in 1N and 3N HCl solutions were carried out using a Teflon reaction vessel maintained at 150°C over 150 days. We obtained high concentrations of Ir and Os, in relatively low pH, high oxygen fugacity and highly saline conditions. For instance, Ir concentration in a solution with 3N HCl as the starting condition reaches about 1,800 ppm, and Os concentrations in solutions with 1N and 3N HCl as the starting conditions reach, in both cases, about 800 ppm. These high concentrations of Ir and Os are believed to be due to the stable existence of Ir⁴⁺ and Os⁴⁺ chloro-complexes in the solution which was clarified by UV and visible absorption spectra, and due to degassing of H₂ from the system, which gives a rise to the decomposition of H₂O. On the basis of the results of the present experimental work and those on the platinum dissolution in HCl solution obtained by Honma et al., we suggest that if the conditions for the formation of hydrothermal origin of Pt-group metals deposits are present, conditions of low pH, high Cl⁻ concentration and oxygen fugacity are favorable for the formation of Pt-group metals, and chloro complexes of Pt-group metals are stable in the ore fluids.

KEY WORDS: Dissolution, Ir, Os, Hydrothermal Reaction, HCl Solution

1. Introduction

Ir and Os are generally insoluble in aqueous solutions. In fact, Ir is the most resistant of the Pt-group metals (PGE) to chemical and electrochemical corrosion²⁾³⁾. Previous studies indicated that Ir and Os are not transported as a fluid phase under low-temperature (<300°C) hydrothermal conditions in nature, but so far no experimental study on the solubility of Ir and Os in hydrothermal conditions have been carried out.

Experimental studies on the solution geochemistry of Ir and Os have not been carried out, probably due to their very low solubilities in aqueous solutions. Eh-pH diagrams for Ir-S-O-H and Os-S-O-H systems at 25°C and 1 bar have been constructed by Brookins⁴⁾. However, few thermochemical data on Ir and Os chloro-complexes are available⁵⁾.

On the other hand, previous studies have reported that some PGE deposits may be of hydrothermal origin^{6)~11)}.

For example, High PGE concentrations of inferred hydrothermal origin were reported by Kucha¹²⁾ in the Polish Kupferschiefer which contains up to 700 ppm Pt, 400 ppm Pd, 600 ppm Ir and 1,100 ppm Au.

Analytical results of studies of Salton Sea geothermal waters by McKibben et al.¹³⁾ have also suggested that Pt is considerably soluble in acidic, high oxygen fugacity ($fO_2 \approx 10^{-30}$) and highly saline solutions at temperature of 300°C. It is well known that Ir and Os are enriched in PGE deposits.

We carried out experiments on the dissolution of Pt in various HCl solutions at 150°C over 120 days, and showed that Pt dissolves in considerable amounts (6,600 ppm) in 3N HCl solution¹⁾.

The purposes of this paper are to; (1) experimentally determine dissoluble amounts of Ir and Os in 1N and 3N HCl solutions at 150°C after 150 days, (2) consider the mechanism of dissolution of Ir and Os in HCl solutions, and (3) suggest that Ir and Os could be transported as chloro-complexes under low temperature hydro-

thermal condition in nature.

2. Experimental

The present experiments on Ir and Os dissolution were carried out using Ir and Os pure metal (99%) powders and 1N and 3N HCl solutions as starting materials.

Four runs, placing the system Ir and Os metals in each of 1N and 3N HCl solutions, were carried out. In each run, 50.0 ml of an HCl solution was placed into a Teflon reaction tube (13 cm long, 3 cm diameter, 0.5 cm in wall thickness) together with about 1.0 g Ir and Os metal powder. Each set of conditions is shown in **Table 1**.

The reaction tube was sealed with air, enclosed in a stainless steel casing, and placed in an electric furnace, the temperature of which was controlled at 150 ± 3°C for a period of 150 days. At the end of runs, the tubes were air-cooled to room temperature.

3. Result and Discussion

After 150 days, each sample solution had a unique color (Table 1). Run #1 and #2 sample solutions were pale yellow with reddish tint and reddish blown in color, similar in appearance to those of dilute and

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Table 1 Experimental system and Ir and Os concentration in solution.

run number	solution (ml)		weight of starting material (g)		Ir (ppm) in solution	Os (ppm) in solution	solution colour
	start	end	Ir	Os			
#1 1N HCl	50.0	40.0	1.0	—	18 ± 1.8	—	pale yellow with reddish tint.
#2 3N HCl	50.0	37.5	1.0	—	1,800 ± 180	—	reddish brown
#3 1N HCl	50.0	43.5	—	1.0	—	810 ± 81	yellow
#4 3N HCl	50.0	45.0	—	1.0	—	780 ± 78	yellow

concentrated H_2IrCl_6 solutions, respectively. Sample solutions obtained in runs #3 and #4 were yellow in color, similar in appearance to that of H_2OsCl_6 solution.

The volume of the obtained solutions are shown in Table 1, indicating that the amount of the solutions decreased over the run. In particular, the sample solution of run #2 decreased from 50.0 ml to about 37.5 ml. It was verified that decrease of 1N and 3N HCl solutions with no metal powder only were less than 2.0 ml during the run over 150 days at 150°C. This indicates that no leak takes place if the metal powder is placed in the system. It was found after the run that the Teflon reaction tube had expanded. These factor suggest that gas had escaped from the system during the run.

Ir and Os concentrations of the resultant solutions were analyzed with an ICP-MS (VG Elemental PQΩ).

Fig. 1 Absorption spectrum curves of the sample solution.

The results are shown in Table 1. The Ir concentration values for final solutions were 18 ± 1.8 ppm (run #1) and $1,800 \pm 180$ ppm (run #2) and the Os final concentration values for the solutions in runs #3 and #4 were both about 800 ppm. These results are reproduced within the limits of 10% by check experiments. Such high concentrations of Ir and Os in HCl solutions have not previously been reported. The present study is the first experimental one to show that Ir and Os are soluble in hydrothermal solutions.

Several stable Ir and Os chloro-complexes in chloride solutions have been reported. For instance, IrCl_6^{2-} , IrCl_6^{3-} , OsCl_6^{2-} , OsCl_6^{3-} and OsCl_6^{3-} may be stable^{2,3,14}.

In order to determine species which are dominant in the final solutions, the nature of the Ir and Os aqueous species in the solutions was studied with UV (Jasco Model UV-TDFO 05) and visible absorption spectra. The results are shown in Fig. 1. The spectra of run #1 and #2 sample solutions appear in a very intense absorption band at 414, 432 and 487 nm. This result showed a similarity to the absorption band of the IrCl_6^{2-} complex obtained by Llopis et al.² and Hamaguchi¹⁵. The spectra of run #3 and #4 sample solutions appear in a very intense absorption band at 335, 342 and 370 nm. This result was similar to the absorption band of OsCl_6^{2-} complex obtained by Larson and Garner¹⁶ and Hamaguchi¹⁵.

These results showed that Ir^{4+} and Os^{4+} chloro-complexes were dominant in aqueous 1N and 3N HCl solutions of this experiment.

Therefore, the following reactions must be taken into account when

considering the dissolution mechanisms of Ir and Os in HCl solutions.

However, regardless of the formation of the chloro-complexes of Ir and Os reactions (1) and (2) demonstrate that even at given high concentrations of Cl^- and H^+ , if H_2 gas is removed from the system, the reaction shown in those formulas will still occur.

In the present experiment, the removal of H_2 gas from the system may have been the crucial factor in the increased concentrations of Ir and Os in the aqueous chloride solution. This hypothesis is supported by the fact that Teflon tubes are permeable with regard to H_2 gas¹⁷, and that in such cases tubes expand. In fact the expansions of the Teflon tubes were observed by the present study. Thus, the higher the concentrations of Ir and Os, the less the guarantee of quality of the post-experimental solutions. If H_2 gas is lost, $f\text{O}_2$ usually rises, according to the following reaction.

It is thought from reactions (1) ~ (4) that Ir and Os are highly soluble as Ir and Os chloro-complexes under conditions of relatively high $f\text{O}_2$ (or low $f\text{H}_2$), when other conditions (temperature, pH, Cl^- concentration) are constant.

Although exact estimates of $f\text{O}_2$ and $f\text{H}_2$ values are difficult to determine, it is certain from UV and visible absorption spectra data that Ir and Os exist as Ir^{4+} and Os^{4+} not Ir^{3+} and Os^{3+} , in-

dicated relatively high fO_2 (or low fH_2) conditions. Recently, Mountain and Wood⁵⁾ and Honma et al.¹⁾ concluded that Pt may be transported as chloro-complexes in very acid and oxidized fluids. The results of fluid inclusion studies on host minerals in PGE deposits¹⁸⁾¹⁹⁾ provide confirmation that a fluid phase is a necessary part of some Pt enrichment processes. Watkinson and Melling¹¹⁾ have suggested that Pt-group minerals (e.g. sperrylite $PtAs_2$, kotulskite $PdTe$, temagamite Pd_3HgTe_3 , sopcheite $Pd_3Ag_4Te_4$) of Salt Chuck Intrusion in Alaska were precipitated from chloride-rich solutions at the temperatures, as below the 300°C to 400°C range. Ir and Os are present as solid solution in Pt-group minerals.

If it is correct that Pt is transported by hydrothermal solution, it is also possible that Ir and Os are hydrothermally transported. The present experiments support this hypothesis.

The previous researches and of the present experiments on Ir and Os dissolutions in HCl solutions at 150°C suggested that Ir and Os may be transported as chloro-complexes in hydrothermal solutions under conditions of

relatively low pH, high Cl^- concentration and fO_2 . Thus, it may be suggested that Ir and Os could be enriched in some hydrothermal deposits such as in hydrothermal PGE deposits.

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Reference

- Honma, H., Shikazono, N. and Nakata, M.: Mining Geol., Vol. 42, p. 259–261, (1992)
- Llopis, J., Gamboa, J.M. and Menendez, V.: Collection Czechoslov. Chem. Commun., Vol. 36, p. 528–533, (1971)
- Ozaki, A., Nakahara, M., Yasumori, I., Ishimori, T. and Iida, I.: Chemistry and application of precious metal elements, p. 519, (1984), Koudansya (Tokyo)
- Brookins, D.G.: Eh-pH diagrams for geochemistry, p. 176, (1988), Springer-Verlag (Berlin, Heidelberg, New York)
- Mountain, B.W. and Wood, S.A.: Econ. Geol., Vol. 83, p. 492–510, (1988)
- McCallum, M.E., Loucks, R.R., Cooley, E.F. and Doerge, T.A.: Econ. Geol., Vol. 71, p. 1429–1450, (1976)
- Rowell, W.F. and Edgar, A.D.: Econ. Geol., Vol. 81, p. 1272–1277, (1986)
- Gunn, A.G., Leake, R.C. and Styles, M.T.: Platinum-group elements mineralization in the Unest ophiolite, Shetland, British Geol. Survey Mineral Reconnaissance Program Rept., Vol. 73, p. 1–116, (1985)
- Mihalik, P., Jacobsen, J.B.E., and Hiemstra, S.A.: Econ. Geol., Vol. 69, p. 257–262, (1974)
- Beal, L.H.: Nevada Bur. Mines Bull., Vol. 63, p. 1–96, (1965)
- Watkinson, D.H. and Melling, D.R.: Econ. Geol., Vol. 87, p. 175–184, (1992)
- Kucha, H.: Econ. Geol., Vol. 77, p. 1587–1591, (1982)
- McKibben, M.A., Williams, A.E. and Hall, G.E.M.: Econ. Geol., Vol. 85, p. 1926–1939, (1990)
- Griffith, W.O. and Raub, C.J.: Gmeline Handbuch der Anorganischen Chemie (Kruft Swars, eds.), p. 183, (1980), Springer-Verlag (Berlin, Heidelberg, New York)
- Hamaguchi, H.: J. Chem. Phys., Vol. 69, p. 569–578, (1978)
- Larson, L.L. and Garner, C.S.: J. Am. Chem. Soc., Vol. 76, p. 2180–2181, (1954)
- Clements, J.D. and McKibben, M.A.: Hydrothermal Experimental Techniques (Ulmer, G.C. and Barnes, H.L., eds.) p. 121–140, (1987), John Wiley and Sons (New York)
- Ballhouse, C.B. and Stumpf, E.F.: Contr. Mineralogy Petrology, Vol. 94, 193–204, (1986)
- Nyman, M.W., Sheets, R.W. and Bonder, R.J.: Can. Mineralogist, Vol. 28, p. 629–638, (1990)

150°Cでの1Nおよび3N塩酸溶液におけるIrおよびOsの溶解*

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1Nおよび3N塩酸溶液におけるIr およびOsの溶解実験を、テフロン反応容器を用いて、150°C, 150日間にわたって行った。結果として、pHが非常に低く、 fO_2 と塩濃度が高い条件のもとで、Irおよび O_2 の高濃度の溶解が起こった。例えば、Irは、3N塩酸溶液(調整時)では約1,800ppmの濃度を示した。また、Osは、1Nおよび3N塩酸溶液(調整時)ではどちらも約800ppmの濃度を示した。

このようなIrおよびOsの高濃度の溶解の要因は、紫外線・可視光線の吸収スペクトルにより明らかになった塩酸溶液中で安定な Ir^{4+} および Os^{4+} のクロロ錯体の存在と、 H_2O の分解によって生じた H_2 ガスの系からの逃散による fO_2 の上昇によるものと推定される。

本研究と、Honma et al. (1992) による塩酸溶液におけるPtの溶解に関する実験的研究により明らかにされた、低pH、高 Cl^-

濃度および高 fO_2 の条件は、熱水性PGE鉱床の形成に有効であると考えられる。

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