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Chromian Aluminian Magnetite and Two Rhodium Alloys in a Platinum Nugget from Goodnews Bay, Alaska

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Abstract

Chromian aluminian magnetite and two rhodium alloys occur in a platinum nugget collected from Clara Creek, south of Goodnews Bay, Alaska. The magnetite contains 9.5 percent Al_2O_3, nearly 20 percent Cr_2O_3, and appears to be the first magnetite of undoubted homogeneity containing so much aluminum in association with chromium. One rhodium alloy is white and shows only slight optical anisotropy; the other is brownish and strongly anisotropic. Both yield identical primitive cubic X-ray patterns, but the brown one may be noncubic (slightly tetragonal?). Iron-bearing platinum, native osmium, erlichmanite, grossular and partially-serpentinized clinopyroxene are also present in the nugget.

Owing to the high temperature of crystallization of platinum metals from a melt, iron-bearing platinum and the rhodium alloys are presumed to have formed at more moderate temperatures, perhaps being mobilized then concentrated locally during host-rock serpentization. The chromian aluminian magnetite may have been produced at the same time, by complete alteration of preexisting chromite.

Introduction

The nugget was collected in 1963 by John P. Brooks, of San Jose, California, during operation of an elevated sluice box on Clara Creek (a tributary of the Salmon River), south of Goodnews Bay, Alaska. The general area of occurrence is described by Mertie (1940). Minerals of special interest are chromian-aluminian magnetite and two kinds of rhodium-bearing alloy.

Description

The nugget is about 7 mm long and roughly equant, but irregularly shaped. In the unmounted hand sample silicate material could definitely be distinguished from platinum metal, the latter making up most of the nugget. A polished section (the one used for analysis) is shown in Figure 1. Large white areas are iron-bearing platinum. Needles of native osmium are present in the interior of platinum grains, but are most easily seen near grain edges. Two small (5 × 10 micron) grains of erlichmanite (Snetsinger, 1971) are associated with native osmium at the edges of platinum grains. The rhodium-bearing alloys form a discontinuous rim around one of the grains of platinum. The lowermost "Rh" symbol in Figure 1 indicates a light grey area; just to the left of this may be seen a very small white area, almost as highly reflecting as the platinum. These represent the two varieties of rhodium alloy. One is white ("rhodium-white") with high reflectance. Nearly all grains of this type are optically isotropic; a few, however, appear to show slight anisotropy in air. The other alloy type is brownish and has lower reflectivity; it is invariably strongly anisotropic, the effect being similar to a section of molybdenite cut parallel to the *c*-axis. Although large (up to 100 × 100 microns) optically homogeneous areas of each rhodium alloy variety are present, the more typical occurrence is as an intimate, equigranular, unoriented, occasionally vermicular intergrowth of the white alloy in the brown one on a 2-micron and smaller scale. The low-reflectance light-grey areas just to the left of the left-hand "Os" symbol are grossular; the mineral is intergrown with platinum. Light grey equant grains at the right side of Figure 1 are magnetite. This mineral is optically homogeneous, the whitish appearance of it near the upper right corner of the figure being due to varying exposure in the original composite photograph. One magnetite grain is, however, slightly—but distinctly—anisotropic. Considering its composition, the magnetite shows abnormally low reflectance, more like that of chromite than magnetite or iron-rich chromite. The abundant low-reflectance silicate minerals are clinopyroxene (high relief) and serpentine. An epoxy-type mounting medium surrounds the nugget.

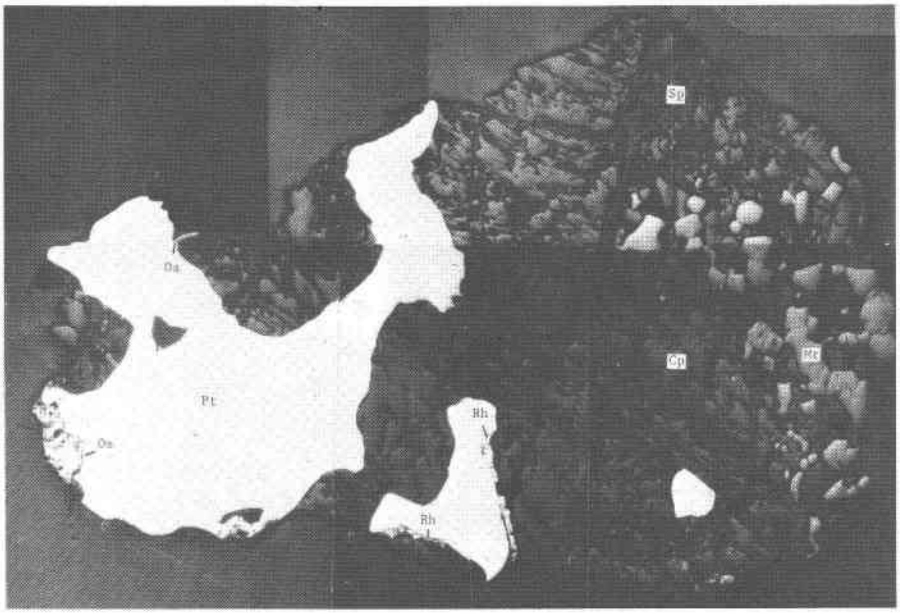

FIG. 1. Composite photograph of nugget; ×20, reflected light. Os = native osmium; Pt = iron-bearing platinum; Rh = rhodium alloy; Sp = serpentine; Cp = clinopyroxene, Mt = chromian aluminian magnetite.

Analytical Procedure

In preliminary qualitative work with the minerals, strip chart scanning was done with a Materials Analysis Company model 400 electron probe. Energy-dispersive qualitative determinations were also made, with lithium-drifted silicon detectors, using Kevex units in conjunction with the MAC probe and a Japan Electron Optics Company JSM-U3 scanning electron microscope, the latter being operated in static beam mode. Under the conditions employed, elements present at the 0.3 wt percent level or higher would have been detected.

An ARL-EMX electron probe, operated at 20KV, was used in quantitative chemical analysis of the minerals. With rhodium and elements of higher atomic number, Lα lines were used; Kα lines were used elsewhere. For the clinopyroxene, serpentine, and grossular, it was possible to find standards close enough to the samples in composition so that no corrections other than instrumental ones were necessary. The magnetite was analyzed with a chromite standard of known composition; matrix corrections were applied, except for the atomic number effect. A synthetic alloy having Pt 91.29, Fe 8.17 (Pt_3Fe) was used for Pt and Fe in the iron-bearing platinum; a natural osmium alloy, and a commercially available synthetic alloy containing Pt 80, Ir 20 (wt percent) were used as standards for, respectively, Os and Ir in the analysis of iron-bearing platinum. No matrix-effect corrections were made. Pt 80, Ir 20 was used for determination of Ir in the native osmium, but for Os in this mineral, a low-porosity briquette containing Os 89.73, Pd 10.27 (wt percent) was used.

Lacking standards of the appropriate composition, attempts were made to synthesize alloys similar to the rhodium-bearing ones. Despite rapid melting and quenching of powdered-metal briquettes by electron beam melting methods, these efforts were unsuccessful owing to selective vaporization of components having lower boiling points. Recourse was therefore made to pure elements for standardization of Rh, Fe, Cu, and Ir in the alloys. Because of matrix effects, this has led to analytical inaccuracy (probably as much as ±10 percent of the amounts determined), even though all matrix-effect corrections were applied. Consequently the data on the rhodium-bearing alloys are given only to two significant figures.

An example of type erlichmanite was the Os, S and Rh standard for erlichmanite in the nugget; pure Fe was used to determine iron. Matrix-effect corrections were not made, which leads to satisfactory data except for a possible slight negative error in Fe. The results are somewhat approximate in any case, owing to the small size of the grains.

Instrumental (background, drift, and deadtime) corrections were always made to the raw data on the minerals, and matrix-effect calculations, when made, were done by computer using Frazer's (1967) data in the mass absorption calculation, and Wittry's (1964) formula for secondary fluorescence effects. Duncumb and Reed's (1968) backscatter-effect results were used in the atomic number calculations. The program used the format of Frazer *et al.* (1966).

Most of the rhodium-alloy intergrowth texture is barely resolvable optically, so in order to be sure of absence of intergrowth in the large areas analyzed, these were examined with the JEOLCO JSM-U3 scanning electron microscope. At a magnification of 3,000 in the back-scattered electron mode (using 25 KV electrons) the two alloy types could readily be distinguished even where most intimately intergrown, and homogeneity of the areas analyzed was verified. Examination (10,000 power, 25 KV) in the secondary electron mode was carried out after attempting to create relief on the sample by soaking in hydrochloric, sulfuric and nitric acids, and mixtures thereof. No textural inhomogeneities were noted in the chemically analyzed alloy areas, but the alloys were quite resistant to the severe etching, and all details of texture may not have been revealed at the higher magnification. Both SEM approaches yielded information from sample depths no greater than 50 Å, and must therefore be considered surficial in nature. The analyzed alloy areas did, however, show slight inhomogeneity within and among themselves under the electron beam; these X-ray intensities represent data from deeper sample levels, and it may be that part of the variation was due to interference of radiation from one alloy underlying another.

Determination of the small amount of Cu present in both rhodium alloys is subject to error, owing to coincidence of Ir LL (1.541 Å) with the CuKα analytical line (1.542 Å). A line ratio correction method analogous to that used for titanium by Snetsinger *et al.* (1968) was applied to the data. The IrLα/IrLL ratio was used. At the low Cu level of the brown alloy no great accuracy is claimed for this procedure; it does, however, enable an improved estimate of Cu.

X-ray powder diffraction film data was obtained for chromian aluminian magnetite and the rhodium alloys. A film-shrinkage correction was made. Filtered CrKα, FeKα, and CuKα radiation were used for the rhodium, with cameras having diameters of 114.59 and 57.3 mm; exposure times were up to 40 hours with helium purging. For the magnetite, CuKα radiation was used, the grain analyzed being small enough so that film darkening due to fluorescence of Cr and Fe did not occur, despite 40 hours exposure without helium purging. A 114.59 mm camera was used. All X-ray data were reduced with the least squares computer refinement program of Evans *et al.* (1963).

Chromian Aluminian Magnetite

Analysis of the magnetite is given in Table 1 together with a structural formula. The latter is admittedly speculative, because (1) the Fe_2O_3/FeO ratio is calculated, and (2) there is no supporting evidence that some of the cations do in fact occupy sites assigned to them. An inverse spinel structure was assumed. The formula is not charge balanced, having 63.52 instead of 64.00 positive charges. This is presumably due to deficiency in the calculated ferric iron. No attempt was made to adjust for this.

Although one of the magnetite grains is slightly anisotropic, the mineral shows no chemical variation from grain to grain or within single grains. Other homogeneous magnetites containing appreciable aluminum, but apparently only trace amounts of chromium, have been noted by Fleischer (1965) and Lewis (1970). Regarding Cr_2O_3, Palache *et al.* (1944) suggest that earlier magnetite analyses showing more than about 1.5 percent are probably of material of doubtful purity. There thus appears to be no satisfactory published analysis comparable to the present one. Boone and Fernandez (1971) have, however, noted that groundmass magnetite in many Azores volcanics contains about 18 percent Cr_2O_3; they do not mention Al_2O_3 content. A magnetite intergrown with ilmenite in a basalt from Arizona contains close to 5 percent Cr_2O_3 and less than 2 percent Al_2O_3 (T. E. Bunch, pers. comm., 1972). In addition, one of the altered chrome-spinels studied by Frisch (1971) with an electron probe showed as little as 28.8 percent Cr_2O_3 and 14.0 percent Al_2O_3.

TABLE 1. Analysis of Chromian Aluminian Magnetite

Oxide	Weight percent	Numbers of metals (32 $O^=$)
Al_2O_3	9.5	3.14
Cr_2O_3	19.9	4.41
Fe_2O_3*	33.9	7.16
TiO_2	3.0	0.63
MgO	5.4	2.26
FeO	27.0	6.33
MnO	0.3	0.07
	99.0	

Suggested structural formula:

$$\overbrace{(Fe^{+3}_{6.71}Ti_{0.63}Fe^{+2}_{0.66})}^{+3}\left[\overbrace{(Fe^{+2}_{5.67}Mg_{2.26}Mn_{0.07})}^{+2}\ \overbrace{(Al_{3.14}Cr_{4.41}Fe^{+3}_{0.45})}^{+3}\right]O_{32}$$

*Calculated on the basis of 24.00 metal atoms per unit cell; Fe as FeO is 57.5 percent.

X-ray diffraction data obtained from a 50-micron magnetite crystal are in Table 2. Most lines of typical magnetite are present, absences presumably being due to the small, single-crystal nature of the material X-rayed. Cell edge is 8.330 ± 0.003 Å, cell volume 578.00 ± 0.07Å^3 and calculated density 4.79 gm/cc.

TABLE 2. X-Ray Diffraction Data for Chromian Aluminian Magnetite

hkl	I/I$_0$	d(calc.)Å	d(meas.)Å
111*	40	4.809	4.82
220*	75	2.945	2.95
311*	100	2.512	2.51
222*	30	2.405	2.41
400*	65	2.083	2.08
422*	20	1.700	1.70
333 511	80	1.603	1.60
440	40	1.473	1.47
533*	20	1.270	1.27
553 731	10	1.085	1.09
800	10	1.041	1.04
844	30	0.850	0.855

*Starred reflections are those used by computer in final least squares iteration. Calculated d-spacings are from refined cell edge a 8.330±0.003Å. Intensities are visual, and approximate because of spottiness of film.

Question may arise as to the appropriateness of calling the mineral magnetite. *Chrome spinel* seems inappropriate because there is insufficient aluminum or magnesium, and chromium is too low for *chromite* or *ferritchromit*.

The Two Rhodium Alloys

Chemical data on these are in Table 3. Fe is the most abundant element in the white alloy, based on numbers of metals. The brownish alloy contains more Rh than the white one: thus the optically more rhodium-like type contains less of that element. Analyses of platinum-metal alloys recorded by Palache *et al.* (1944) contain a maximum of 11 percent Rh (for an iridosmine; p. 112); the alloys studied here therefore appear to be the most rhodium-rich ones so far encountered. Presence of copper in them is not unexpected; at least, Stumpfl and Clark (1965) found the element repeatedly in their iron-bearing platinum from Borneo.

Initially, X-ray diffraction data were obtained using one hand-picked, apparently optically homogeneous single grain of each alloy. These gave identical X-ray patterns: primitive cubic with *a* 2.979 ± 0.001Å. To verify this result, because of possible intergrowth, a second apparently optically homogeneous grain of each alloy was picked out. Film patterns were obtained, and both were identical to each other and to the first pair of films. Then these grains were studied with Cr, Fe, and Cu radiation in small (57.3 mm) and large (114.59 mm) cameras, with and without helium purging, at exposure times up to 40 hours. No differences in lines present or in their spacing and intensities were detected. Although the intergrowth question cannot be completely eliminated, it appears possible that the alloys each have the same X-ray pattern. Conceivably, however, the brown alloy is slightly noncubic (tetragonal, with *a/c* close to 1.00?), but why this should be the case is presently not clear. The strong anisotropy of the brown alloy is also not easily explained; neither is the difference in reflectance from the white one.

X-ray data, applicable to both alloys, are in Table 4. The cell edge lengths (2.979Å) are comparable to the value 2.987Å found by de Bergevin and Muldawer (1961) for primitive cubic synthetic $Rh_{0.53}Fe_{0.47}$. These authors do not list *d*-spacings; observed spacings for the rhodium-bearing alloys are most similar to those of the primitive cubic equiatomic synthetic alloy OsV (JCPDS-PDF card no. 18-947; Dwight, 1959), which has nearly the same cell edge and relative line intensities. Two primitive cubic reflections (*hkl's* 311 and 320) are, however, unaccountably absent from the rhodium alloy data.

Alloy grains ranging in size from 50 to 100 microns in largest dimension were used for X-ray study, yet smooth, unspotted lines appeared on the films. This suggests, in agreement with the tentative high-magnification SEM results, that individual domains reflecting X-rays are of micron or sub-micron size in these alloys.

Assuming *Z* = 1.00, calculated density of the brownish alloy is 6.2 gm/cc, and the white type has 5.7 gm/cc. In Figure 2 the rhodium-bearing alloys are plotted on an Fe-Rh-Ir triangular compositional diagram. Information is available only for the binary synthetic alloy systems; unknown ternary synthetic compounds and structural types probably exist, and Figure 2 is not to be taken as a ternary diagram.

TABLE 3. Analyses for the Two Rhodium Alloys

Metal	Weight percent	Numbers of metals on basis 1.0 per unit cell
	Brown rhodium alloy	
Rh	48	0.5
Fe	24	0.4
Ir	26	0.1
Cu	0.3	0.01
Total	98.3	
	White rhodium alloy	
Rh	44	0.4
Fe	32	0.5
Ir	24	0.1
Cu	1.3	0.02
Total	101.3	

TABLE 4. X-Ray Diffraction Data for Both Rhodium Alloys*

hkl	I/I_o	d(meas.)Å	d(calc.)Å
100*	15	2.98	2.979
110	100	2.115	2.107
111*	<2	1.720	1.720
200	25	1.493	1.490
210	5	1.34	1.332
211	80	1.22	1.216
220	2	1.06	1.053
300, 221*	2	0.993	0.993
310	5	0.946	0.942
222*	<2	0.860	0.860
321	10	0.798	0.796

*Starred reflections are those used by computer in final least squares iteration. Intensities and d-spacings of lines apply to both alloys. I/I_o values are visual. Calculated d-spacings are from refined cell edge a 2.979±001Å.

Despite the necessarily diminished accuracy of analysis, and the question of tetragonality of the brown alloy, there is no doubt that both alloys represent previously undescribed natural phases; one or both of them should at some future date be named. No effort in this direction is made now, however; further natural occurrences and more synthetic examples will have to be studied before a satisfactory nomenclature can be devised.

Iron-Bearing Platinum and Accessory Minerals

The iron-bearing platinum is homogeneous and approximates Pt_3Fe, having Pt 88.9, Fe 9.5, Os 0.8, Ir 1.6, summation 100.8 wt percent. Awaiting refinements in naming minerals in the Pt-Fe system—*cf.* discussion of the problem by Cabri (1972)—this alloy has here simply been referred to as iron-bearing platinum.

Native osmium gives Os 83.6, Ir 15.3, summation 98.9 percent. No other elements were detected, but the extremely high atomic number resulted in high analytical background, and elements present in amounts somewhat higher than 0.3 wt percent may have been missed during qualitative scans. The analysis was carried out on the largest (20 × 100 microns, *ca*) osmium lath available, but smaller ones seemed comparable in composition. Any alloy that contains greater than 80 wt percent Os is called native osmium by Hey (1963), and this definition is used here. Other occurrences of the metal, analyzed qualitatively by Lévy and Picot (1961), contain up to 98 percent Os, the remainder being mainly Ir.

This nugget contains the third occurrence of erlichmanite, the others having been dealt with earlier by the writer (Snetsinger, 1971). The mineral has Os 69, Fe 4, Rh 3, and S 25, summation 101 wt percent. It contains iron, whereas the type minerals did not. Ir, Ru, and Pd were not detected and are less than 0.3 wt percent; they were above that value in the previous occurrences.

The serpentine contains SiO_2 36.7, Al_2O_3 2.7, FeO 12.3, MgO 37.2, and H_2O (by difference to 100.0) equals 11.1 wt percent; calcium was looked for but not found. The clinopyroxene has SiO_2 51.6, Al_2O_3 3.1, FeO 4.0, CaO 25.0, MgO 17.0, summation 100.7. These silicates exhibited slight inhomogeneities but no particular effort was made to refine this observation. Grossular was identified by X-ray diffraction and optics, supplemented by qualitative probe work. It appears to be nearly pure grossular, as no Fe, Mg, or Mn were detected.

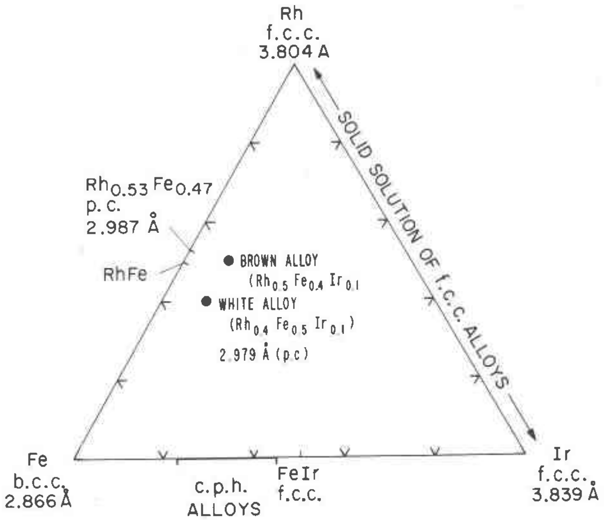

FIG. 2. Triangular (not ternary) diagram showing composition of the rhodium-bearing alloys in relation to what is known of the Rh-Fe, Rh-Ir, and Fe-Ir synthetic binaries. p.c. = primitive cubic, f.c.c. = face-centered cubic, b.c.c. = body-centered cubic, c.p.h. = close-packed hexagonal. Data on c.p.h. alloys after Raub *et al.* (1964). Intermediate Rh-Fe alloy result is from de Bergevin and Muldawer (1961). Structural data on the pure metals are from Barrett and Massalski (1966).

Origin

Iron-bearing platinum and the rhodium alloys probably did not crystallize from a melt because of the high temperature (*ca* 2000°C) that would be involved. Elements necessary for their formation may have been transported and localized by fluids available during sepentinization of the host rock. This must have been a relatively low-temperature (<500°C?) process, although the writer cannot be precise about the temperature, pressure, or chemistry involved The rhodium alloys are assumed to have been deposited later than the platinum, because they partially mantle it. Conceivably the native osmium lamellae developed in the platinum by exsolution from the latter at low temperatures.

Chromian aluminian magnetite has physical properties and a chromium content that are intermediate between pure magnetite and the altered chromite (ferritchromit) described by, among others, Beeson and Jackson (1969), and Engin and Aucott (1971). Formation of ferritchromit has in most instances been attributed to late-stage, low-temperature alteration accompanying sepentinization or chloritization of silicates in the host rock. It is suggested by analogy that the chromian aluminian magnetite may have formed by complete alteration of preexisting chromite during the same alteration that produced partial serpentinization of the associated clinopyroxene, and mobilized the platinum metals.

Acknowledgments

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