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OSARSITE, A NEW OSMIUM-RUTHENIUM SULFARSENIDE FROM CALIFORNIA

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ABSTRACT

Osarsite from placer gravels at Gold Bluff, Humboldt Co., California has the simplified formula (Os,Ru)AsS; electron probe analysis gives Os 35.6, Ru 18.1, Ir 2.0, Ni 0.9, Pt 0.4, Pd 0.6, Rh 0.2, S 11.5, and As 30.6, summation 99.9 weight percent. Osmium metals in the formula are slightly in excess of ruthenium, and the As/S ratio is 1.14. Indexing of X-ray reflections on the basis of a monoclinic (arsenopyrite-type) cell gives a 5.933 ± 0.001, b 5.916 ± 0.002, c 6.009 ± 0.002 Å, and β 112°21′ ± 02′. Assuming $Z = 4$, calculated density is 8.44 gm/cc. X-ray data from synthetic OsAsS, RuAsS and $Os_{0.5}Ru_{0.5}AsS$ strongly resemble those of osarsite. The mineral is defined as a sulfarsenide in which osmium is the most abundant cation.

INTRODUCTION

Osarsite (name and definition approved by the Commission on New Minerals and Mineral Names, I. M. A.) is an osmium-ruthenium sulfarsenide, one 150-micron grain of which, associated with irarsite, occurs in a portion of California State Division of Mines sample 9508, platinum placer sands from Gold Bluff, Humboldt County, California. The name is for its composition, and osarsite is defined as a sulfarsenide in which osmium is, on the basis of numbers of metals, the most abundant cation. This "majority cation" nomenclature is used following the example of Genkin *et al.* (1966; see also Fleischer, 1967) in connection with irarsite. Type material and some osmium-ruthenium sulfarsenides synthesized by the writer are, through the courtesy of P. E. Desautels, deposited in the mineralogy collections, Smithsonian Institution (U. S. National Museum number 123218). Pronunciation is äz-ärs-īt, accent being on the first syllable.

PHYSICAL DATA

The author regrets that facilities at hand did not permit determination of the microhardness or reflectivity of osarsite. Qualitatively, however, the mineral is gray in reflected light, and appears to have a reflectance similar to irarsite—judging from the description of the latter by Genkin *et al.* (1966). Anisotropy in air is weak but distinct, the effect being slightly less than that of (say) iridosomine under crossed nicols. Because the osarsite grain was a single discrete one in a platinum-metal sand sample, its hardness relative to other minerals is impossible to estimate. The mineral forms a rudely flamboyant polycrystalline intergrowth, the curved laths of which are 100–150 microns long and 30 microns wide. As the irarsite occurred beneath the polished surface of a portion of the grain, occurrence of it with the osarsite was detected only by electron probe and X-ray diffraction analysis. Textural relations between the two minerals are unknown.

ANALYTICAL PROCEDURE

The analysis was done with an ARL-EMX model electron probe, and Os, Ru, Ir, Ni, Pt, Pd, Rh, As, and S were determined. Standards were, for As, Ni, Pd, and Pt: pure metals. Pt 90 percent Rh 10 percent, and Pt 80 percent Ir 20 percent (artificial alloys) were Rh and Ir standards; pure synthetic PbS was used for sulfur. A natural alloy containing Os 33.8, Ru 29.8, Ir 27.9, Pt 4.0, Pd 2.8, Rh 1.7 and Fe 0.2 weight percent (Snetsinger, 1971a) was used for the Os and Ru determination. Matrix-effect correction procedures are as described elsewhere (Snetsinger, 1971b). Ordinarily arsenic would have been measured with the $K\alpha$ line at 1.18 Å, but a series of $\mathrm{Os}L\beta$ lines occupies the range from 1.16 to 1.22 Å, so As $L\alpha$ was used. With the exception of Ni and S, for which $K\alpha$ radiation was used, the other elements were determined with $L\alpha$ lines. Measurements were made at 20 KV.

CHEMICAL DATA

Analysis of osarsite is given in column 4 of Table 1, together with the formula (column 5) derived from the analysis. Steps in the calculations are given (columns 2 and 3) to illustrate the extent to which the data are modified by matrix-effect corrections. Sum of all the cations is 2.10 instead of 2.00, presumably a result of analytical error. The As/S ratio of 1.14 is, however, outside any error involved, and considered due to substitution of As for S. Osmium is barely in excess of ruthenium. Elements other than those reported were below the detection limit, which is estimated to have been 0.1 weight percent under the conditions employed. Owing to interference with the overlying material, a satisfactory analysis of the irarsite could not be obtained. It can only be characterized as having (on the basis of As + S = 10.0) the approximate chemical formula:

$$\mathrm{Ir_{3.5}(Pt,\ Pd,\ Rh)_{0.6}Ni_{0.6}As_{5.4}S_{4.6}}.$$

In establishing this formula, all Os, Ru, As, and S due to osarsite were

TABLE 1. CORRECTION DATA AND ANALYSIS OF OSARSITE[1]

(1) Element	(2) Data corrected for drift, background, & deadtime	(3) Data in (2) corrected for mass absorption, fluorescence	(4) Data in (2) corrected for mass absorption, fluorescence, and atomic number	(5) Formula on basis As + S = 4 calculated from data in (4)	
Os	32.8	32.5	35.6	0.98	2.10
Ru	16.6	16.3	18.1	0.93	
Ir	1.7	1.7	2.0	0.05	
Ni	1.0	1.0	0.9	0.09	
Pd	0.4	0.5	0.6	0.03	
Pt	0.3	0.3	0.4	0.01	
Rh	0.2	0.2	0.2	0.01	
As	25.0	30.7	30.6	2.13	4.00
S	7.8	10.3	11.5	1.87	
Totals	85.8	93.5	99.9		

[1] For details of matrix-effect correction procedure, see Snetsinger, 1971b. Measurements done at 20 KV.

subtracted from the analysis. By comparison, Genkin *et al.* (1966) give their type irarsite as:

$$Ir_{1.45}Ru_{1.13}Rh_{0.84}Pt_{0.78}As_{5.6}S_{4.4}.$$

The small, compositionally variable area of the grain underlain by irarsite was scrupulously avoided in the osarsite probe determinations, and analyzed osarsite areas were quite homogeneous. It is therefore strongly suggested that the small amount of Ir recorded (Table 1) is in the osarsite structure, and not due to analytical interference with irarsite.

X-RAY PROCEDURE

X-ray diffraction data were obtained from the 150-micron osarsite grain using Ni-filtered Cu radiation. Exposure was 40 hours in a He-purged 114.59 mm camera. A film shrinkage correction was made. Data on related synthetic compounds are from diffractometer tracings standardized with pure Si. Ni-filtered Cu radiation was used; scanning speed was 1° 2θ per minute at one inch per minute chart speed. The pattern of natural osarsite contains additional lines which correspond to the intergrown irarsite; using data of Genkin *et al.* (see also XRDF card #19-591) these are easily identified and substracted. Although the remaining lines are spotty, their intensities and relative positions are similar to corresponding reflections of arsenopyrite (Morimoto and Clark, 1961); the osarsite *d*-spacings (and those of the synthetic materials) are therefore referred to a monoclinic, arsenopyrite-type cell. For reduction of X-ray data a number of *d*-spacings were indexed by analogy to arsenopyrite. Then the least-squares unit cell refinement computer program of Evans *et al.* (1963) was used, keeping the indexed reflections fixed, and allowing the program to automatically select indices for the rest of the reflections. The same indices were fixed in natural osarsite and in the synthetic compounds. All *d*-spacings present in each X-ray pattern were used; these amounted to about 65 for osarsite and 40 for the synthetic compounds. Each reflection was assigned equal full weight in the refinement cycles of the program. For each compound roughly half the *d*-spacings were computer-selected for the final iteration of cell refinement, the remainder not being used. In the osarsite data (Table 2), the one index selected by the program for each *d*-spacing during cell refinement is listed. Therefore in a few instances additional, theoretically-feasible reflections, possibly contributing to the intensity of a given line, may have been omitted; moreover, because the osarsite grain was not amenable to single crystal study, some indices which may later prove to be theoretically implausible have perhaps been included. This last situation concerns mainly high-index osarsite reflections and does not affect the final results appreciably, as most *d*-spacings smaller than 1.395 Å were not used in the final cell refinement.

X-RAY RESULTS

Osarsite has *a* 5.933 ± 0.001, *b* 5.916 ± 0.002, *c* 6.009 ± 0.002, *β* 112°21′ ± 02′ and cell volume 195.1 ± 0.2 Å^3. Assuming Z = 4, calculated density is 8.44 gm/cc. Refined cell parameters for synthetic

TABLE 2. X-RAY DATA FOR NATURAL OSARSITE AND SYNTHETIC RuAsS

Natural Osarsite[1]				Synthetic RuAsS[2]
hkl	I/I_0	*d*(calc.)Å	*d*(meas.)Å	*d*(meas.)Å
110(F)	10	4.023	4.03	4.03
$\bar{1}11$(F)	100	3.801	3.79	3.79
---	---	----	---	3.47(2)
020^*	50	2.958	2.96	2.96
---	---	----	---	2.89(<2)
?	5	----	2.81	---
002	60	2.779	2.78	2.78
200(F)	70	2.744	2.74	2.74
$\bar{1}12^*$	5	2.659	2.66	2.65
---	---	----	---	2.61(<2)
$\bar{1}21$(F)	50	2.541	2.54	2.55
012^*	30	2.515	2.51	2.52
$\bar{2}02^*$	40	2.480	2.48	2.49
$\bar{2}12$	25	2.287	2.28	2.28
102(F)	30	2.169	2.17	2.16
$\bar{2}21$(F)	20	2.087	2.09	2.09
---	---	----	---	2.02(30)
220	60	2.012	2.01	2.01
$\bar{3}02$	100	1.894	1.892	1.890
$\bar{3}11^*$	80	1.873	1.870	1.868
$\bar{1}31$(F)	60	1.833	1.832	1.832
$\bar{3}12^*$	30	1.804	1.806	1.810
013(F)	25	1.768	1.769	1.762
122^*	20	1.749	1.751	1.748
131(F)	60	1.694	1.696	1.696
202^*	50	1.662	1.661	1.658
$\bar{3}21^*$	5	1.642	1.641	----
$\bar{2}23^*$	10	1.604	1.604	1.606
103^*	50	1.582	1.583	1.588

Table 2. (continued) X-RAY DATA FOR NATURAL OSARSITE AND SYNTHETIC RuAsS

Natural Osarsite[1]				Synthetic RuAsS[2]
hkl	I/I_o	*d* (calc.)Å	*d*(meas.)Å	*d*(meas.)Å
301	5	1.569	1.565	----
320	5	1.556	1.553	----
311*	5	1.517	1.517	----
231*	25	1.455	1.455	1.450
123*	30	1.395	1.395	1.392
---	---	----	----	1.363(<2)
$\bar{1}24$	40	1.329	1.328	1.324
232	35	1.271	1.269	1.268
420*	15	1.245	1.244	----
133	15	1.234	1.236	1.231
411	30	1.202	1.203	----
---	---	----	----	1.196(5)
---	---	----	----	1.173(5)
340	25	1.150	1.150	1.151
$\bar{5}11$	45	1.142	1.141	1.139
$\bar{4}33$*	20	1.132	1.131	(Reflections corresponding to smaller *d*-spacings not recordable by diffractometer for synthetic RuAsS)
151*	20	1.115	1.115	
$\bar{2}51$	20	1.098	1.098	
015*	35	1.092	1.092	
$\bar{2}52$	5	1.068	1.069	
$\bar{1}44$	40	1.049	1.048	
$\bar{4}41$	40	1.042	1.042	
520*	5	1.029	1.029	
224	25	1.018	1.018	
$\bar{2}53$	20	1.006	1.005	
060	20	0.986	0.986	
$\bar{6}12$	25	0.974	0.973	
$\bar{1}61$*	25	0.967	0.967	
530	25	0.959	0.960	
144	50	0.950	0.950	
$\bar{2}61$	10	0.935	0.935	
$\bar{1}54$	10	0.926	0.926	
205	10	0.916	0.916	
$\bar{4}35$	20	0.899	0.899	
$\bar{6}15$	40	0.882	0.882	
360*	25	0.868	0.868	
601	25	0.852	0.852	
611	30	0.843	0.844	
$\bar{5}53$	20	0.827	0.827	
271	30	0.787	0.787	
$\bar{2}37$	30	0.784	0.783	
733*	40	0.778	0.778	

[1] Film data. "F" after index indicates it was held fixed during computer cell refinement; starred indices were in addition selected by and used by the computer for final iteration of least-squares refinement. Horizontal lines indicate reflections observed with synthetic RuAsS but not in osarsite. The *d*-spacings are calculated from refined cell parameters given in text. See text for experimental method.

[2] Diffractometer data. Numbers in parentheses after *d*-spacings are intensities, taken proportional to peak height, of reflections not observed in osarsite. These are relative to the 3.79Å *d*-spacing (I/I_o = 100). Intensities of other reflections are similar to osarsite and are not listed. Horizontal lines indicate spacings observed with osarsite but not in RuAsS. The *d*-spacings are calculated from refined cell parameters given in Table 3. Reflections from spacings smaller than 1.139Å could not be recorded adequately by diffractometer. See text for experimental method.

OsAsS, $Os_{0.5}Ru_{0.5}AsS$ and RuAsS are in Table 3, but for reasons given below only data on synthetic RuAsS are listed in detail for comparison with osarsite (Table 2). Although its X-ray reflections can be accounted for on the basis of a monoclinic cell, there is a slight chance osarsite may be triclinic, with α and γ angles very near 90°. At least, Morimoto and Clark (1961) found that, when the As/S ratio is less than 1.2, single crystal X-ray methods indicated arsenopyrite is triclinic. Some analogous effect may exist with osarsite, but proof of it must await occurrences of adequate single crystal material.

SYNTHESIS

Hulliger (1964) has previously made OsAsS and RuAsS, and obtained X-ray data on them. He does not list d-spacings but does give cell parameters. The present writer has synthesized OsAsS, and RuAsS, and $Os_{0.5}Ru_{0.5}AsS$ by sintering briquettes containing appropriate amounts of the finely-powdered pure elements for several days in sealed, evacuated quartz-glass tubes at 900°C. No attempt was made to freshly reduce the ruthenium or osmium. A faint odor of H_2S was noted upon opening each of the tubes, suggesting that, despite briquetting the powders under vacuum and evacuating the tubes while sealing them, a trace of water remained. Synthetic $Os_{0.5}Ru_{0.5}AsS$ was less well-crystallized (*i.e.*, yielded broader X-ray peaks) than the pure Os or Ru end members, probably because of difficulty substituting two cations into similar structural positions in a reasonably short time. In addition, a few weak ($I < 5$) lines, tentatively ascribed to Os metal, were found in both synthetic osmium-bearing compounds. Diffractometer patterns obtained were, however, in all three cases similar to each other and to that of natural osarsite, down to the minimum d-spacing value (about 1.14 Å) adequately recordable by the diffractometer. Because the synthetic RuAsS more probably approached

TABLE 3. X-RAY PARAMETERS OF SYNTHETIC OSMIUM-RUTHENIUM SULFARSENIDES

Present Paper					
Compound	a(Å)	b(Å)	c(Å)	β	Cell Volume(Å^3)
OsAsS	5.964±0.005	5.925±0.004	6.006±0.003	112°02′±03′	196.7±0.2
$Os_{0.5}Ru_{0.5}AsS$	5.992±0.007	5.944±0.004	6.044±0.003	113°05′±05′	198.0±0.2
RuAsS	5.945±0.006	5.920±0.005	6.025±0.007	112°55′±05′	195.3±0.2
Hulliger's (1964) Data					
OsAsS	5.94	5.92	6.01	111°54′	197
RuAsS	5.95	5.92	6.02	113°07′	194

stoichiometry than did the OsAsS, and showed better crystallinity than $Os_{0.5}Ru_{0.5}AsS$, it is chosen for X-ray comparison with natural osarsite (Table 2). Refined cell dimensions of all three synthetic compounds are, however, given in Table 3; several reflections possibly due to osmium metal were eliminated in obtaining these data. With the exception of $Os_{0.5}Ru_{0.5}AsS$ (the cell parameters of which are anomalously enlarged, presumably the result of disorder), agreement of the current data with Hulliger's (1964) results is reasonable (Table 3). One or more of the cell edges might have been expected to increase slightly with substitution of the larger (0.69 Å) Os^{4+} cation for Ru^{4+} (0.67 Å; ionic radii from Smith, 1963). Ignoring $Os_{0.5}Ru_{0.5}AsS$, no such trend is clearly indicated by the data groups, but β does decrease with increasing Os, and cell volume increases as a result.

DISCUSSION

As in the present study, Hulliger (1964) found that OsAsS and RuAsS have the arsenopyrite structure; but he has also studied other synthetic platinum-metal compounds of the MAsS type (Hulliger, 1963; Hulliger and Mooser, 1965) and has noted that when M is Rh, Ir, Pd, or Pt, the cobaltite structure prevails. Irarsite and hollingworthite [(Rh, Pd, Pt, Ir)AsS; Stumpfl and Clark, 1965] are natural examples of this type.

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