On the Distribution of Major and Trace Elements Between Metal and Phosphide Phases of Some Iron Meteorites

K. P. Jochum, M. Seufert, and F. Begemann
Max-Planck-Institut für Chemie, Mainz, Germany

Z. Naturforsch. **35a**, 57–63 (1980); received October 25, 1979

Dedicated to Prof. Dr. H. Hintenberger on the occasion of his 70th birthday

The concentrations of Fe, Ni, Co, P, Cu, Ga, Ge, Mo, Ru, Rh, Pd, W, Ir and Pt in the phosphides and the metal of the coarse octahedrites Campo del Cielo, Canyon Diablo, Cranbourne and Sardis, the coarsest octahedrite São Julião de Moreira and the hexahedrites Braunau and Lombard have been determined by spark source mass spectrometry. Striking differences are observed of the element contents between bulk meteorite and the phosphides as well as between the different phosphide modifications schreibersite and rhabdite. Extreme values are a 20 fold depletion of Ga and a 40 times higher content of Pd in the phosphides. A particularly strong correlation between the noble metal element content and size of phosphide aggregates is observed; it is shown that this correlation is not an artifact of the sample preparation but that is must be real.

Introduction

Most iron meteorites contain schreibersite and rhabdite [1]. Both minerals have the same chemical formula $(Fe, Ni)_3P$ and the same crystal structure; they are simply morphological variants. Schreibersite occurs as large, rather angular crystals up to several centimeters in size while rhabdite is of regular rhombohedral shape and has much smaller dimensions. The crystals range from sub-micron to some tens of microns in diameter, they appear like needles or rods (rhabdos = rod).

Both minerals are of secondary origin; they form upon the exsolution of phosphorus from the metal phase during cooling. According to Clarke and Goldstein [2] massive schreibersite forms above 850 °C while rhabdite appears only at lower temperatures of around 600 °C. As the distribution coefficient of elements between metal and phosphides, as well as their diffusion coefficient within both these phases, are temperature dependent the occurence of these phosphides in iron meteorites is of particular interest. Randich and Goldstein [3] and Kulpecz and Hewins [4] have used them for unraveling the cooling histories of meteoritic parent bodies using Ni as Leitelement.

Little is known whether or not other elements might be used with advantage as well. This question has been adressed only seldom and therefore multielement analyses of phosphides are scarce. The only such study appears to have been that of Hermann et al. [5] who have investigated the distribution of some trace elements between schreibersite and metal of the octahedrites Canyon Diablo and Odessa.

As a first step of a more thorough investigation we have determined the major and trace elements in schreibersite, rhabdite and in the metal of the octahedrites Canyon Diablo, Campo del Cielo, Cranbourne, São Julião de Moreira, Sardis and of the hexahedrites Braunau and Lombard.

Experimental Procedure

The measurements were performed by spark source mass spectrometry (SSMS). The preparation of the samples is outlined in Figure 1. Chunks of the meteorites were treated with 4 N hydrochloric acid. After several days when the reaction had come to a halt the solution was heated gently until all metal had dissolved. The residue was obtained by centrifuging and the phosphides were separated from this residue by means of a hand magnet. Schreibersite and rhabdite were separated from one another on an inclined plane according to their different shape. Rather clean fractions could be obtained in this way (Fig. 2a–c) which, in their X-ray diffraction pattern, showed only the lines of $(Fe, Ni)_3P$. Furthermore, in Sardis schreibersite was abundant enough so that in addition to a sample

Reprint requests to Dr. K. P. Jochum, Max-Planck-Institut für Chemie, Saarstr. 23, D-65 Mainz.

0340-4811 / 80 / 0100-0057 $ 01.00/0. — Please order a reprint rather than making your own copy.

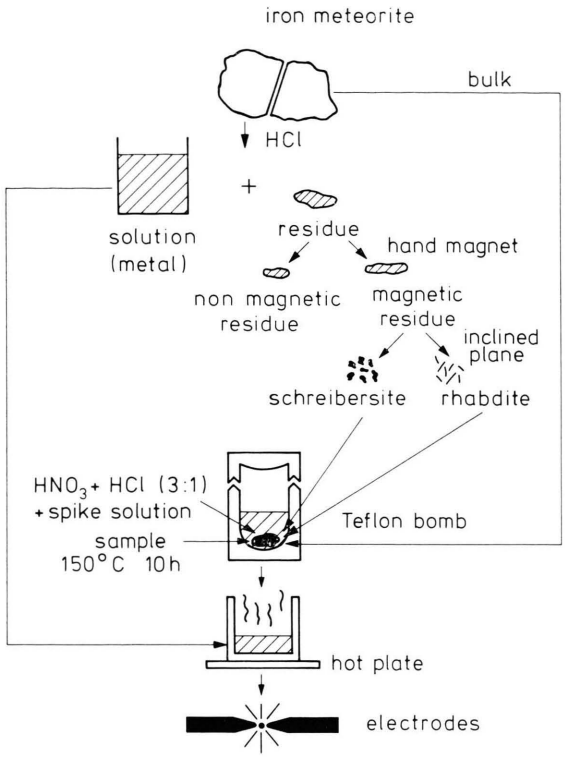

Fig. 1. Schematic course of sample preparation.

prepared chemically as outlined in Fig. 1 another one has been analyzed which was separated mechanically.

The phosphides were dissolved in a Teflon bomb in a mixture of nitric and hydrochloric acid (10 hours at 150 °C) and spikes of isotopically enriched solutions were added to enable the determination of the concentrations by isotope dilution. A second piece of each meteorite was dissolved in one step by treating it directly with HNO_3 + HCl in the Teflon bomb. This was taken to be the bulk sample.

The solutions were taken to dryness in a Teflon beaker. A few drops of HNO_3 were added repeatedly to the nearly dry samples in order to convert them to nitrates or oxides which produce simple mass spectra. The powders were finally mixed with ultrapure graphite and then briquetted into rod shaped electrodes for sparking in the ion source. The amount of salts per electrode corresponded to as little as 5 mg sample which, in most instances, was, however, only a small aliquant of the total amount available.

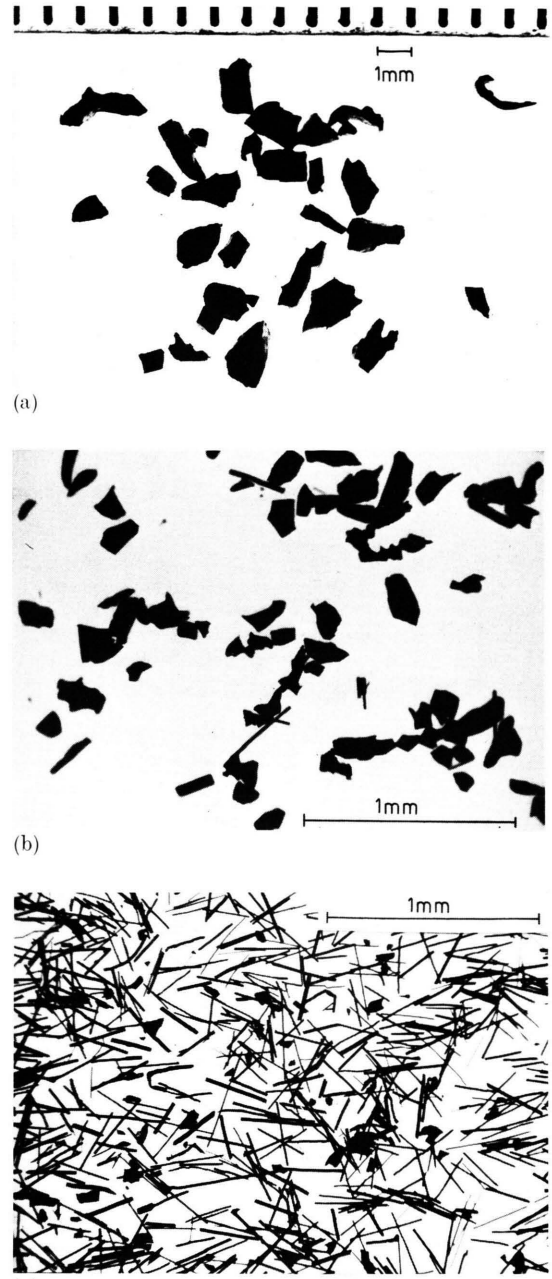

Fig. 2. Phosphides from the coarse octahedrite Canyon Diablo obtained by chemical separation: a) coarse schreibersite, b) fine schreibersite, c) rhabdite.

A spark source mass spectrograph Type AEI MS 702 was used for this work [6—8]. Two techniques were utilized for ion detection:

photographic registration with complete elemental coverage and high resolution, and

electrical detection by magnetic peak switching, which results in a better precision on a restricted number of elements.

The major elements were measured with the electrical ion detection system. An on-line computer (HP 9825 A) controls the magnetic field and processes the data. On each mass ion currents were registered by a multiplier until a total charge of 1 nCb had been collected at a monitor. About 50 integrations were performed on each mass taking the elements in rotation.

Trace elements were usually analyzed using photoplate detection. Because of the high resolution of this method the lines of polyatomic ions were generally separated from the isotopes of the trace elements. Four to eight Ilford Q 2 photoplates with 15 exposures each, ranging from 0.001 to 1000 nCb, were taken so that for each isotope about 10 measurements could be performed. Line densities were recorded automatically by a Steinheil photometer.

The concentrations of Cu, Ga, Ge, Mo, Pd, W, and Pt were determined via the isotope dilution method using isotopically enriched samples of ^{65}CuO, $^{71}Ga_2O_3$, $^{73}GeO_2$, ^{98}Mo, ^{108}Pd, $^{183}WO_3$, and ^{194}Pt. Ru, Rh, Ir, and the major elements Fe, Ni, P, and Co were measured using relative elemental sensitivity factors as determined from the analysis of Ventron standard solutions which were treated in the same manner as the sample solutions. This assures that matrix effects such as type of chemical bonding or sample mineralogy are minimized.

Results and Discussion

The data obtained on five octahedrites and two hexahedrites are compiled in Tables 1 and 2. Table 1 lists the bulk compositions and, for the two hexahedrites, that of kamacite which for the present purpose is defined as being the HCl soluble fraction of the meteorites. For comparison the data of other investigators have been included. Note, however, that agreement can be expected only for the major elements Fe and Ni and those minor or trace elements (Co and Ga) which are not strongly enriched in the phosphide minerals (see below). For these the agreement is seen to be good.

In Table 2 are given the results for the various phosphide phases investigated till now. Our specimens of São Julião de Moreira and Sardis contained only very little rhabdite so that no data on its chemical composition are available. Lombard, in addition to the rod-shaped rhabdite proper, contained some plate-shaped phosphides which, although a *contradictio in adjecto*, are generally referred to as rhabdite as well [1].

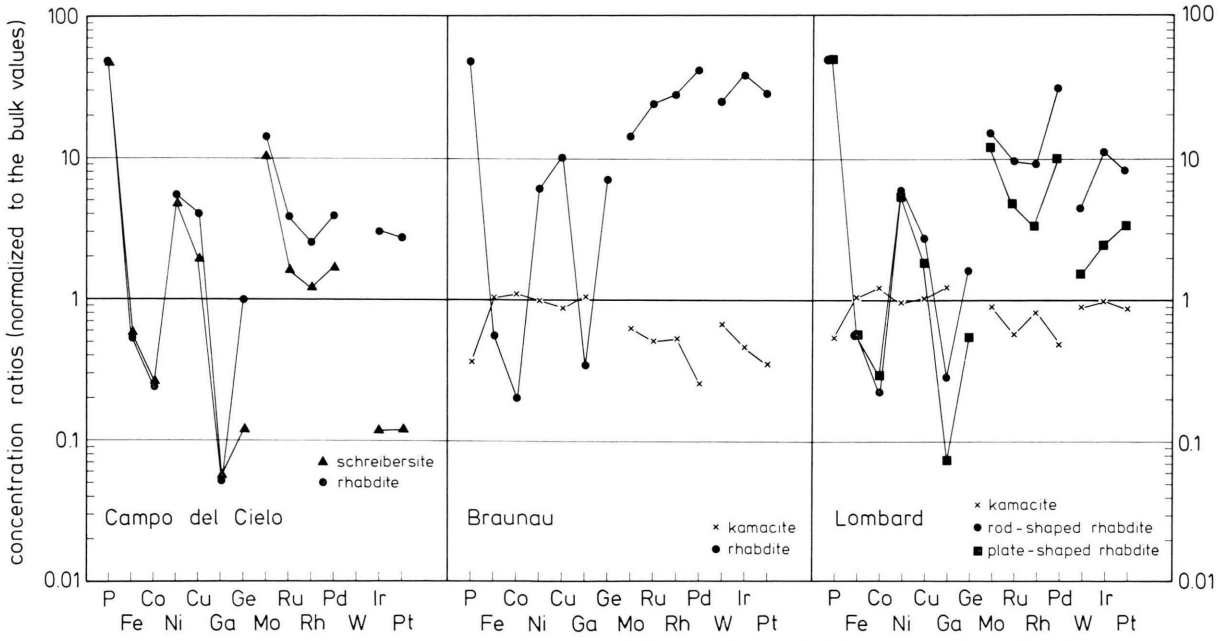

Fig. 3. Concentration ratios of major and trace elements in different phases of 3 iron meteorites. The data are normalized to the bulk.

Table 1. Concentration of major and trace elements in the bulk of 7 iron meteorites and the kamacite of 2 hexahedrites. For comparison the data of other authors are included ([1], except for Mo and Pd, which are from [9]). The precision for P, Ru, Rh and Ir is better than ± 10 percent, for all other elements better than ± 4 percent.

Meteorite	Group		Fe [%]	Ni [%]	Co [%]	P [%]	Cu [ppm]	Ga [ppm]	Ge [ppm]	Mo [ppm]	Ru [ppm]	Rh [ppm]	Pd [ppm]	W [ppm]	Ir [ppm]	Pt [ppm]
Campo del	I	SSMS	92.3	6.65	0.42	0.31	110	92	420	7.3	12	2.1	5.4		4.0	9.0
Cielo	Og	Lit.		6.62—	0.43	0.25	109	83	392	7.8			3.7		3.2	9.7
				6.74				90	421						3.9	
Canyon	I	SSMS	92.4	6.83	0.46	0.25	120	85	320	9.8	7.3	1.3	4.2	3.6	3.1	7.9
Diablo	Og	Lit.		6.98—	0.39—	0.26	125—	74—	283—	7.4			3.6		1.9	8.0
				7.40	0.51		157	81.8	324						2.0	
Cranbourne	I	SSMS	92.4	6.90	0.42	0.30	150	91	360	10	6.2	1.2	3.6	0.9	2.6	7.2
	Og	Lit.		6.74—	0.48—	0.25	119—	74—	262—	5.0			4.8		1.8	
				7.34	0.53	0.26	120	85.4	358							
Sardis	I	SSMS	91.6	6.70	0.49	1.1	100	85	380	15	6.3	1.3	3.3	1.7	2.1	9.7
	Og	Lit.		6.58	0.47	0.24		93.7	400						1.3	
				6.69												
São Julião	IIB	SSMS	92.5	6.65	0.49	0.24	100	49	120	5.8	2.5	1.4	2.9	0.37	<0.2	1.5
de Moreira	Ogg	Lit.		~6.4	0.47	0.9	79	35—	73—						0.0093	2.9
							90	46.2	107						0.012	
Braunau	IIA	SSMS	93.8	5.40	0.42	0.31	140	67	200	7.9	34	2.9	2.7	2.9	13	35
bulk	H	Lit.		5.21—	0.44—	0.24	131	56.5	183						11	
				5.52	0.92		700	61.5							12	
kamacite		SSMS	94.1	5.30	0.46	0.11	120	69		4.9	17	1.5	0.68	1.9	6.2	12
Lombard	IIA	SSMS	93.5	5.70	0.44	0.30	120	60	180	6.0	18	2.2	2.1	1.7	2.6	22
bulk	H	Lit.		5.59—	0.42	0.28		58	174						2.3	
				5.75												
kamacite		SSMS	93.7	5.60	0.50	0.16	120	70		5.1	10	1.8	1.0	1.5	2.3	19

Table 2. Concentration of major and trace elements in schreibersite and rhabdite of 7 iron meteorites. The P concentration corresponds with a stoichiometric value of about 15%. The precision for Ru, Rh and Ir is better than ± 10 percent, for all other elements better than ± 4 percent.

Meteorite	Group	Phosphide phase	Fe [%]	Ni [%]	Co [%]	Cu [ppm]	Ga [ppm]	Ge [ppm]	Mo [ppm]	Ru [ppm]	Rh [ppm]	Pd [ppm]	W [ppm]	Ir [ppm]	Pt [ppm]
Campo del Cielo	I Og	Schreibersite	52.5	32.1	0.11	210	5.5	49	75	19	2.6	9.1	0.60	0.48	1.1
		Rhabdite	48.9	35.8	0.10	440	5.1	410	99	45	5.3	21	2.6	12	24
Canyon Diablo	I Og	Schreibersite coarse (Fig. 2a)	62.4	22.1	0.24	140	2.1	63	76	18	2.9	6.8	0.57	0.51	1.9
		Schreibersite fine (Fig. 2b)	53.6	31.0	0.17	260	5.8	100	44	24	4.0	26	0.43	4.3	22
		Rhabdite (Fig. 2c)	39.4	45.1	0.079	570	9.4	190	87	31	5.7	55	1.4	10	58
		Schreibersite (Hermann et al. [5])	66.27	16.03	0.255				37.0	7.67				0.05	
Cranbourne	I Og	Schreibersite	48.5	36.1	0.10	290	13	110	56	14	1.9	10	0.45	0.47	1.0
		Rhabdite	38.2	46.6	0.070	1300	34	2100	150	78	11	43	4.0	20	47
Sardis	I Og	Schreibersite (chem. sep.)	61.0	24.0	0.24	82	2.7	61	55	17	2.8	5.8	0.77	0.65	2.7
		Schreibersite (mech. sep.)	60.5	24.7	0.17	210	3.1	120	69	17	3.4	7.6	0.72	0.76	4.3
São Julião de Moreira	II B Ogg	Schreibersite	67.5	17.0	0.16	190	1.4	12	37	3.2	1.5	3.3	0.20	<0.1	0.56
Braunau	II A H	Rhabdite	51.6	33.0	0.083	1400	23	1400	110	830	81	110	72	490	980
Lombard	II A H	Rhabdite (rod-shaped)	51.7	33.2	0.093	320	16	290	87	170	20	65	7.7	28	180
		Rhabdite (plate-shaped)	52.8	32.2	0.12	210	4.2	98	71	84	7.2	21	2.6	6.1	77

With very few exceptions the data from the two tables are internally consistent within the limits of error anticipated from the accuracies for the individual elements.

As is immediately apparent the distribution of the elements between the phosphide phases and the bulk is very irregular. This is depicted in Fig. 3 where the concentration ratios — normalized to the bulk values — are plotted. (The elements are arranged with increasing atomic number.) Certain elements (Fe, Co, Ga) are strongly depleted in the phosphides, others (Ni, Cu, Mo, Ru, Rh, and in particular Pd) are even more strongly enriched. The effects are especially pronounced in the hexahedrites which contain very little or no schreibersite. Finally, there are Ir and Pt which, at least in the octahedrites, show a peculiar behaviour in that they are enriched in the rhabdite but depleted in the massive schreibersite.

For all elements but Mo and W there is a clear correlation between concentration and grain size. This is shown in Fig. 4 for Ni, Co, and Ir; it actually is observed even for the two rhabdite modifications from Lombard. It is gratifying to see that in these plots the results of Hermann et al. [5] fall into line; from the position of their data points on these curves it would appear that the schreibersite they analyzed was very coarse grained.

The observed grain size dependance of the concentration together with the fact that the noble metals are the ones showing the highest enrichment in the phosphides made us suspect that we might be measuring an artifact. If these elements were residing in an acid-soluble phase, went into solution during the chemical preparation of the phosphides and were subsequently electrochemically deposited on the residue then the same correlation between concentration and grain size would be anticipated since the specific surface area available for such a deposition increases with decreasing size of the aggregates.

In order to test for this possibility a sample of schreibersite was separated mechanically from Sardis and analyzed. The results are shown in Figure 5. Considering the difficulties in having samples with the same grain size the agreement is satisfactory. Most important in the present context is that there are no systematic differences in the concentrations which depend on the nobleness of the elements. From this we conclude that the

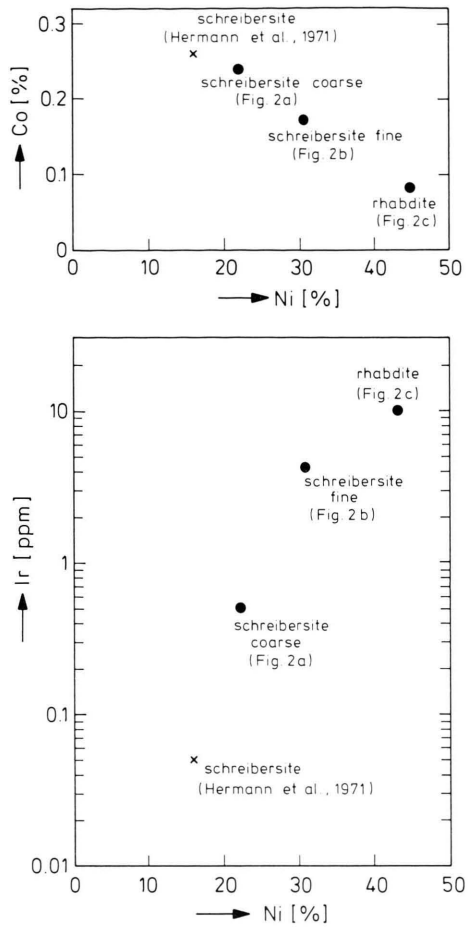

Fig. 4. Correlation between Ni, Co and Ir in phosphides of different grain sizes in Canyon Diablo.

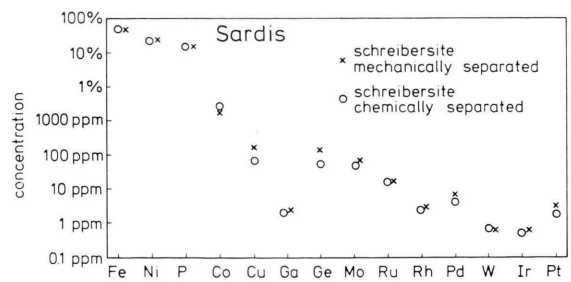

Fig. 5. Concentration of elements in two schreibersite samples from Sardis which were separated mechanically (×) and chemically (○), respectively.

observed grain size dependance of the concentration of trace elements is real.

It remains to be seen whether or not this observation can be developed into a quantitative tool by correlating it with the thermal histories of the

meteorite parent bodies. For Ni, where the size dependance of the concentration has been known since long [10—12], such attempts have been met with some success [3, 4]. It is not immediately apparent whether or not it is beneficial that some of the trace elements show a range of concentrations which is from one to two orders of magnitude larger than that of Ni.

Acknowledgements

We are grateful to Drs. E. P. Henderson and J. McNally for supplying us with the iron meteorite samples. We thank Mrs. S. Best and Mrs. C. Sudek for their help with the preparation of the samples and the mass spectrometric measurements, Mr. S. Specht for the micro-photographs and Dr. Dr. F. Wlotzka for the X-ray analyses.

[1] V. F. Buchwald, Handbook of Iron Meteorites, University of California Press, Berkeley 1975.
[2] R. S. Clarke Jr. and J. I. Goldstein, Smithsonian Contrib. Earth Sci. No. 21 (1978).
[3] E. Randich and J. I. Goldstein, Geochim. Cosmochim. Acta **42**, 221 (1978).
[4] A. A. Kulpecz Jr. and R. H. Hewins, Geochim. Cosmochim. Acta **42**, 1495 (1978).
[5] F. Hermann, W. Kiesl, F. Kluger, and F. Hecht, Mikrochim. Acta Wien 225 (1971).
[6] G. D. Nicholls, A. L. Graham, F. Williams, and M. Wood, Anal. Chem. **39**, 584 (1967).
[7] S. R. Taylor, Geochim. Cosmochim. Acta **29**, 1243 (1965).
[8] H. Hintenberger, Fortschr. Mineral. **54**, 141 (1977).
[9] A. A. Smales, D. Mapper, and K. F. Fouché, in: Origin and distribution of the elements (Ed.: L. H. Ahrens), Pergamon Press, Oxford 1968, pp. 329.
[10] E. P. Henderson and S. H. Perry, Proc. U.S. Nat. Mus. **107**, 339 (1958).
[11] J. I. Goldstein and R. E. Ogilvie, Geochim. Cosmochim. Acta **27**, 623 (1963).
[12] S. J. B. Reed, Geochim. Cosmochim. Acta **29**, 513 (1965).