Reports

Phosphide from Metorites: Barringerite, a New Iron-Nickel Mineral

Abstract. *Schreibersite, (Fe,Ni)$_3$P, and a higher phosphide, barringerite, occur in the Ollague pallasite. The composition of the higher phosphide, determined by electron probe microanalysis, is (Fe$_{0.58}$Ni$_{0.42}$Co$_{0.003}$)$_{1.95}$P. It is hexagonal, with space group* P$\bar{6}$2m *and* a = *5.87 ± 0.07 angstroms and* c = *3.44 ± 0.04 angstroms. If we assume a primary origin, the new mineral indicates that troilite and schreibersite crystallized at high temperatures. The occurrence of a higher phosphide in a pallasite indicates local nonequilibria within a group of meteorites that are remarkable for their overall degree of equilibrium crystallization.*

Many of the iron and stony-iron meteorites contain abundant and large grains of schreibersite, (Fe,Ni)$_3$P. This is the only natural phosphide known, although several higher phosphides have been synthesized (*1–3*). In the course of a study of the pallasitic meteorites—a group characterized by large olivine [(Mg,Fe)$_2$SiO$_4$] crystals set into an Fe-Ni matrix—a new phosphide mineral was observed (*4*). It occurs in the Ollague pallasite (*5*) along the contacts between schreibersite and troilite (FeS). The mineral is named barringerite (*6*) after D. M. Barringer, the early and avid defender of the meteorite origin of the Barringer or Meteor Crater, located near Winslow, Arizona.

The compositions of the barringerite [(Fe$_{0.58}$Ni$_{0.42}$Co$_{0.003}$)$_{1.95}$P] and adjoining schreibersite [(Fe$_{0.64}$Ni$_{0.36}$Co$_{0.003}$)$_{2.9}$ P] were determined by replicate analyses with the electron probe microanalyzer (Table 1). A spectrometer scan indicates no differences between the two minerals in the content of the minor elements; both contain less than 1 weight percent Co and Mg. No other minor elements were detected. If we assume that the slight deviations from stoichiometry result from experimental uncertainties, these phases can be approximated as M$_2$P and M$_3$P, where M represents metal content.

The barringerite grains are too small to be extracted for x-raying. Individual grains are less than 1 μm in diameter; they occur in bands that are 10 to 15 μm wide and several hundred micrometers long. A composite sample containing the higher phosphide as well as neighboring schreibersite and troilite was sampled with a fine dental drill. The resulting powder was x-rayed in a Debye-Scherrer camera, with CrKα radiation and a vanadium filter. Table 2 lists all of the lines in the resulting pattern, except those that uniquely belong to troilite or schreibersite. The new phase is structurally similar to the synthetic phosphide analogs, Fe$_2$P and Ni$_2$P.

The synthetic analogs are isostructural; they are hexagonal, contain three formula units per unit cell, have a calculated density of 6.90 g/cm^3 (Fe$_2$P), and belong to space group $P\bar{6}2m$ (*2*). It is highly probable that the barringerite has similar characteristics. Its unit cell parameters, computed from all the lines listed in Table 2, are $a = 5.87 \pm 0.07$ Å and $c = 3.44 \pm 0.04$ Å, with $c/a = 0.586$ (*7*). This compares with $a = 5.865$ Å, $c = 3.456$ Å, and $c/a = 0.589$ for synthetic Fe$_2$P and $a = 5.865$ Å, $c = 3.387$ Å, and $c/a = 0.578$ for synthetic Ni$_2$P (*2*). The calculated density of barringerite is 6.92 g/cm^3.

The color of barringerite is very similar to the white of kamacite; it is bluish compared to schreibersite. Barringerite has a slightly higher reflectivity in both air and immersion oil than does schreibersite and a lower reflectivity in air and oil than does kamacite. It is harder than either schreibersite or kamacite. Although the barringerite is noticeably anisotropic (white to blue), bireflectance was not observed.

Data from the binary systems Fe-P and Ni-P indicate that M$_2$P and metal

Table 1. Compositions of adjacent phosphides (in weight percent) measured with the electron microprobe. Iron, Ni, and Co (United Minerals and Chemicals) (at least 99.99 percent purity) and analyzed schreibersite from the Grant meteorite were used as standards. Appropriate corrections for dead time, background, absorption, fluorescence, and atomic number were made.

Mineral	Fe (%)	Ni (%)	P (%)	Co (%)
Schreibersite	52.7 ± 1.1	31.5 ± 0.6	15.8 ± 0.3	0.25 ± 0.03
Barringerite	44.3 ± 0.9	33.9 ± 0.7	21.8 ± 0.4	0.25 ± 0.03

Table 2. X-ray diffraction pattern of barringerite, compared to the standard patterns of Fe$_2$P and Ni$_2$P (*15*). Those values marked with asterisks are uniquely those of the new phosphide; the others overlap with lines of troilite or schreibersite that could not be separated from the sample. Because of these coexisting phases, intensities are not indicated.

Barringerite d (Å)	Synthetic Fe$_2$P		Synthetic Ni$_2$P		*hkl*
	d (Å)	Intensity	*d* (Å)	Intensity	
2.98	2.95	50			110
2.85*	2.86	50			101
2.53	2.55	50			200
2.23	2.24	100	2.21	100	111
2.03*	2.05	100	2.03	80	201
1.88*	1.91	100	1.92	80	120
1.72	1.72	100			002
1.68	1.69	100	1.69	70	300
	1.67	100	1.67	40	121
1.48	1.46	20			220
1.41	1.40	70	1.41	40	310
	1.35	50			221
1.29*	1.30	70	1.30	40	311
1.28	1.28	100	1.27	60	122
1.27	1.27	50			400
1.205	1.21	100	1.19	60	302
1.197	1.19	50			401

cannot coexist stably (*1*, *8*). Iron and Fe_2P can coexist metastably if an Fe_3P melt is quenched, although they will react rapidly to form Fe_3P as soon as the metastable equilibrium is disturbed. In contrast to the Fe-P system, in the Ni-P system there are even intermediate phases—$Ni_{12}P_5$ and $Ni_{\hat{=} 2.55}P$—that preclude stable coexistence of Ni_2P and Ni_3P.

Existing studies of the ternary system provide little additional information on the equilibrium relations between M_2P and M_3P phases. Buchwald, and Doan and Goldstein report no phases more rich in phosphorus than M_3P (*9*). Vogel and Baur (*10*) provide limited information on the observed phase relations, although they do not consider either the $Ni_{12}P_5$ or the Ni_2P phases, or the possibility of a solid solution of Fe_2P-Ni_2P; the latter would be predicted on the basis of the occurrence of the new phosphide. Nevertheless, their results indicate that for melts containing bulk ratios of Fe to (Fe + Ni) greater than 0.33 (this applies to most meteoritic melts), as well as at least 13 weight percent P (this is unlikely in meteorites), the first phase to crystallize from the melt will be Fe_2P. Presumably this should be $(Fe,Ni)_2P$, an indication of the theoretical equilibrium coexistence of Fe-rich M_2P and M_3P phases.

Phosphides in which the ratio of Fe to Ni is that of the natural Ollague phases were synthesized. Appropriate amounts of the elements (*11*) were mixed and heated at 850°C in evacuated silicon dioxide glass tubes for several weeks (during which time the samples were repeatedly reground in order to increase grain contact) and were then quenched and x-rayed. The resulting patterns show a mixture of M_2P and M_3P, a confirmation that for the observed Fe-Ni content the two phases can coexist.

The origin of the new phosphide is unclear. Several characteristics must be considered in attempting to evaluate its formation: (i) its restriction to schreibersite-troilite interfaces and its elongate shape parallel to these contacts (Fig. 1); (ii) its finely polycrystalline character; (iii) its occurrence close to (although nowhere in direct contact with) metal; (iv) its extension, although minor, along fractures. These factors do not permit a clear choice between a high- and a low-temperature origin; both must be considered.

Several considerations suggest a low-temperature origin for the barringerite. The Ollague pallasite cooled very slowly [an average of 0.8°C/10^6 years through the range 700° to 300°C according to Buseck and Goldstein (*12*)], and thus equilibration between coexisting phases presumably had sufficient time to take place. The barringerite is clearly incompatible with metal and yet it occurs as close as 30 μm to kamacite. Reaction would have been retarded if the barringerite had formed at low temperatures. Furthermore, there are minor extensions of the barringerite along microfractures within the schreibersite. Such extensions, although not pronounced in the samples investigated, are typical of weathering products. On the other hand, it is possible that these microfractures were former zones of weakness and thus sites of greater diffusion, thereby explaining the minor elongation of the barringerite in these areas, even at high temperatures.

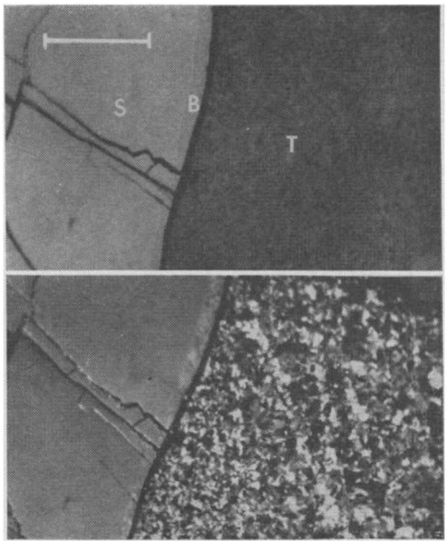

Fig. 1. Narrow band of barringerite crystals (*B*) lying between schreibersite (*S*) and troilite (*T*). Lower photograph was made with the Nicol prisms partly crossed to show the anisotropism and polycrystalline nature of both barringerite and troilite. Scale bar = 150 μm.

If the barringerite were secondarily produced from schreibersite, Fe would have been removed concurrently with the addition of P. The source for the P is problematical—the schreibersite is not noticeably affected by terrestrial weathering, and the metal contains too little P to provide a satisfactory source. Moreover, if this had occurred, it is not clear why the new phase should then have formed only along the troilite contacts.

A high-temperature origin removes the difficulties inherent in explaining the barringerite as a product of terrestrial weathering; it also permits an explanation for its peculiar restriction to the trolite-schreibersite contacts as well as its finely polycrystalline character.

Consideration of the Fe-S and the Fe-Ni-S phase diagrams (*8*, *13*) shows that "troilite" in equilibrium with metal can take more S and Ni into its structure at high than at low temperatures. On cooling from a melt, the "troilite" would have absorbed Fe from its surroundings and released Ni as the temperature decreased. Had it been adjacent to schreibersite, the effect of the troilite reequilibration would have been to enrich the Ni and P content of schreibersite (relatively) while depleting its content of Fe, thereby producing the new higher phosphide. These effects would be localized at the schreibersite-troilite borders and would be chemically consistent with the composition of the barringerite. Such an explanation suggests a high-temperature origin for both troilite and schreibersite.

In response to these chemical changes at the margins of the schreibersite mass, an elemental redistribution occurred within and between the phosphides. Diffusion was presumably possible at the moderate to high temperatures involved. Lattice strains developed within the new phase as a result of the reactions. Even if the barringerite had grown epitaxially, straining and work hardening would have occurred on cooling. Thus, by the time the new phosphide had cooled to room temperature, it would be expected to be finely polycrystalline; this is indeed observed (Fig. 1).

The occurrence of a higher phosphide within a meteorite containing abundant metal is indicative of a metastable condition. This local nonequilibrium, exhibited in a member belonging to a group that otherwise displays a remarkably high degree of internal equilibrium (*14*), is perplexing, provocative, and significant. The microprobe identification combined with the laboratory synthesis of barringerite confirms its character. If, in fact, the barringerite did form at high temperatures, this indicates an origin at elevated temperatures for both troilite and schreibersite. If, on the other hand, it formed as a result of terrestrial weathering, then there are no such restrictions on the origin of the pallasite within which it occurs. In either event, the occurrence of this higher phosphide presents an obvious dilemma in view of our present knowledge of the Fe-Ni-P system and the origin and later history of the pallasite meteorites.

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7. Slightly different values result if only the lines that belong uniquely to the new phase are used. As these lines are few in number, are very weak, and result in relatively large errors, the values of the cell edges that they yield are considered less accurate than those from the entire listed pattern.
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16. I thank Drs. H. Axon, V. Buchwald, J. Goldstein, and M. Hey for useful discussions. F. Wood and G. Scott helped in the laboratory and Dr. Goldstein calculated the microprobe corrections. The Ollague specimen came from the Nininger Meteorite Collection at Arizona State University. Part of the work was done at the NASA Goddard Space Flight Center. Supported by the Research Corporation, Arizona State University Grants Committee, and NSF grant No. GA-1200. Contribution No. 35 from the Center for Meteorite Studies, Arizona State University.

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Potassium Enrichments in Interstitial Waters of Recent Marine Sediments

Abstract. *Potassium enrichments in marine sediments have been reported which would imply a rate of diffusion of potassium into the oceans much larger than any of the know rates of addition or removal by other mechanisms. Experiments with mixtures of seawater and clay suggest that spurious enrichments can be produced if sediment samples are allowed to warm up before the pore water is expressed.*

Potassium ion concentrations in interstitial waters of marine sediments are reported to be enriched relative to the overlying seawater (*1–3*). Shishkina (*1*) summarized detailed analyses of 29 representative cores from the deep oceans and found that in the first half meter of sediment K^+ is enriched relative to Cl^- by 17 percent in red clays, 12 percent in calcareous (*Globigerina*) oozes, and 11 percent in diatom oozes. These sediment types characterize 38, 48, and 14 percent, respectively, of the area of pelagic ocean floor (*4*). One may thus infer a worldwide average potassium enrichment in the first half meter of sediment of about 14 percent.

An average potassium concentration gradient of roughly 0.56 percent per centimeter (taking the average depth of the first half meter as 25 centimeters) bespeaks a very considerable upward flux of potassium ion due to simple diffusion. A similar downward diffusion flux of chloride ion has been estimated by Shishkina (*5*) on the basis of chloride depletions she has found in Black Sea sediments. We have not measured diffusion rates of K^+ ion in mixtures of sediment and seawater, but related measurements have been made by others so that a reasonable estimate is possible. The following factors must be considered.

1) Diffusion coefficients of electrolytes (except H^+) in water at 25°C fall in the range 1 to 2×10^{-5} cm^2/sec (*6*). The most mobile major ions in seawater are K^+ and Cl^-, having self-diffusion coefficients and a joint diffusion coefficient in $0.5N$ electrolyte solutions of about 1.8×10^{-5} cm^2/sec, half again larger than the value for Na^+.

2) The obstructive effect of nonreactive sediment particles on diffusion rates will depend on size-sorting of sediments. With a well-washed fine sand Duursma (*7*) found a self-diffusion coefficient for Cl^- of 5.5×10^{-6} cm^2/sec at 20°C, corresponding (*6*) to about 6.0×10^{-6} cm^2/sec at 25°C, or exactly one-third of the diffusion rate in bulk solution. In sediments of mixed sizes the obstructive effect would be greater.

3) The cation exchange capacity of clay minerals in the sediment will, generally speaking, diminish the rates of transient diffusion of cations (*7*), slightly enhance the rates of steady-state diffusion of cations, and will not affect the rates of independent anion diffusion. During transient diffusion the cation exchange capacity will slow down cation spreading rates by buffering the composition changes even though the actual solution fluxes are undiminished. In steady-state diffusion, by contrast, there are no composition changes; there are only fluxes, and these may even be slightly augmented by the surface mobility of exchangeable cations bound on clay (*8*). We are dealing here with a case of steady-state diffusion in which the cation exchange effects are probably negligible.

Duursma (*7*) measured Cl^- tracer diffusion in a Mediterranean calcareous-clay sediment mixed with seawater and found a diffusion coefficient of 3.5 to 5.5×10^{-6} cm^2/sec at 20°C. These measurements involved only the interdiffusion of Cl^- isotopes. Shishkina (*5*), on the other hand, measured the rate of spreading of sea salt from a high-salinity sediment core to a low-salinity core placed in contact with it and found a diffusion coefficient for Cl^- in Atlantic Ocean cores of 2.4 to 4.3×10^{-6} cm^2/sec. The diffusion of Cl^- in her experiments, although independent of cation exchange, required the joint diffusion of seawater cations that are preponderantly slower than Cl^- (*6*).

The steady-state diffusion rate of K^+ in sediments, if mainly compensated by counterdiffusion of other slower cations, should be nearly equal to the spreading rate of Cl^- as measured by Shishkina. The diffusion of K^+ can be faster, approaching the rate of Cl^- tractor diffusion, if it is compensated instead by joint diffussion of Cl^-.

4) A steady-state diffusion rate at 2°C, a typical temperature at the ocean floor, will be roughly half what it would be in the laboratory at 25°C (*6*). The hydrostatic pressure at a typical depth of 3800 m increases ionic mobilities about 5 percent (*9*).

Taking all these factors into account, we estimate that the diffusion coeffi-