BARRINGERITE FROM THE SANTA CATHARINA UNGROUPED IRON METEORITE.

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Introduction: Barringerite, $(Fe,Ni)_2P$, is a rare higher phosphide, which has been reported only from the Ollague (Imilac) pallasite [1], the lunar meteorite Y 793274 [2], some CM chondrites [e.g., 3], and the oxidation zone of a Cu-Ni sulfide deposit in China [4]. Phase diagrams predict that barringerite can not stably co-exist with Fe,Ni metal and should react with the latter to produce schreibersite [5]. In fact, barringerite has never been observed to co-exist directly with Fe,Ni metal, except for a recently described occurrence in the Onello iron [6]. In this contribution we report on the forbidden barringerite-metal association in the Santa Catharina iron meteorite.

Occurrence: Santa Catharina is a weathered Ni-rich ataxite, which consists of dark and light regions as visible in the reflected light optical microscope [7,8]. Sample #2180 of the Russian meteorite collection, which we studied, contains also such regions. Rare barringerite was discovered in the light areas. It is present as elongated (80-220 µm) thin (5-12 µm) spindles (Fig. 1) set within the metal in two approximately perpendicular directions. No reaction zone is observed at the barringerite/metal contact (Figs. 1,2). Schreibersite is much more abundant than barringerite and occurs as (1) well-shaped rhabdite crystals (20-200 µm in size) rimmed by Fe oxide, and (2) plates or irregular inclusions (30-400 µm) rimmed by swathing kamacite (Fig. 3). Obviously, the Fe oxide could have been formed by oxidation of kamacite during terrestrial weathering. Barringerite and schreibersite were not observed in direct contact with each other. The shortest distance between the two phosphides encountered is about 80 µm. No Fe phosphates as previously described from Santa Catharina [8,9] were found in the specimen. The barringerite and schreibersite occurrences in Santa Catharina are very similar to those previously described from the Onello iron [6].

Mineral Chemistry: ***Barringerite*** in Santa Catharina has an almost uniform chemical composition. No zoning is present within barringerite spindles (Fig. 2). The average (wt.%, standard deviation is in brackets here and below) is: Fe 53.7 (0.73), Ni 22.7 (0.37), Co 2.16 (0.31) P 21.6 (0.34). Si, S, Cr, Ca, Ti, and Mn were not detected. The corresponding formula is $Fe_{1.38}Ni_{0.56}Co_{0.05}P$. The composition of barringerite from Santa Catharina is remarkably similar to that from Onello (Fig. 4). In both irons, barringerites are Co-rich and have a Ni content of about 20 wt%. Barringerites of CM chondrites have variable Ni and Co contents but when they are Co-rich they are also rich in Ni (Fig. 4). In addition, the barringerites from CM chondrites contain commonly some S, Cr and Ca, elements that are absent in the Santa Catharina and Onello barringerites. Pallasite Ollague (Imilac) and lunar meteorite Y 793274 contain low-Co barringerite (Fig. 4). ***Schreibersite*** in Santa Catharina shows a large compositional range: Fe 32-57, Ni 28-49, Co 0.14-0.82 (wt%) with a Co-Ni anti-correlation (Fig. 4) and a constant P content of 15.6 (0.17) wt%. Schreibersite with rhabdite morphology can have any composition within the range, whereas schreibersite plates and irregular inclusions are always Ni-rich (39-49 wt%) and Co-poor (0.14-0.34 wt%). There is no compositional zoning within schreibersites (Fig. 3). Similar compositional variations were documented in the Onello iron (Fig. 4). .***Fe,Ni metal*** has practically the same composition around both barringerite and schreibersite, except for the kamacite rimmed schreibersite. The metal contains (wt%) Ni 29.4 (0.62), Co 0.78 (0.04), P 0.06 (0.03). It is close in composition to the metal phase of the Santa Catharina USNM#6293 sample [8] but poorer in Ni compared to the bulk Ni content [7] accepted for the meteorite. The metal phase of USNM#6293 consists of fcc taenite with domains of tetrataenite [8]. Our sample should contain the same phases because it is similar in composition to USNM#6293. The swathing kamacite around schreibersite (Fig. 3) contains Ni 5.4, Co 1.6, P 0.03 (wt%). No changes of the metal composition at the barringerite/metal boundary is present (Fig. 2).

Discussion: Experimental data [5] show that barringerite is unstable in contact with Fe,Ni metal. However, Fe-P melts with more than 10 wt% P tend to form an unstable eutectic (metal+barringerite) under a high cooling rate [5]. This is the observation that was used to explain the occurrence of barringerite in the Onello iron [6]. However, both Onello and Santa Catharina obviously contain less than 10 wt% P and the morphology of the barringerite indicates precipitation by exsolution from the metal. In contrast to the predictions of the phase diagram [5], barringerite is in complete equilibrium with the Santa Catharina metal because the composition of the phase does not vary and there is no reaction zone at the barringerite/metal interface (Figs. 1,2). On the other hand, the huge compositional range of schreibersite and the kamacite/oxide rim around schreibersite grains (Figs. 3) clearly indicate that schreibersite is out of equilibrium with the metal – similar to what has been observed in other iron meteorites, e.g., [10,11].

It can be suggested, that the phase relationships in the Fe-Ni-P system should be re-studied at high Ni contents and low temperatures. In fact, the Ni content of schreibersite is increasing when temperature is decreasing [12]. However, the stabilization of tetrataenite in Ni-rich metal can restrict Ni diffusion to schreibersite and, therefore, can suppress the schreibersite growth. Under such conditions, precipitation of barringerite is more preferable because barringerite is poorer in Fe,Ni and has a lower Ni/Fe ratio than schreibersite.

Conclusion: Barringerite but not schreibersite can stably co-exist with metal in Ni-rich ataxites at low temperatures. The phosphide apparently exsolved from the metal, possibly in the course of cooling.

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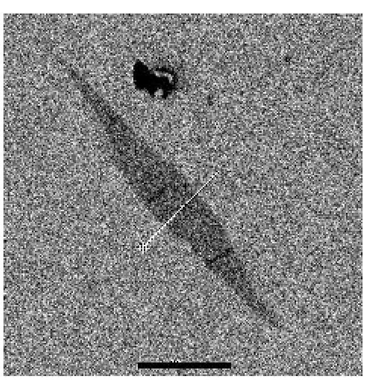

Fig.1. *A barringerite spindle in Santa Catharina (BSE image).The scale bar is 20 ì m.*

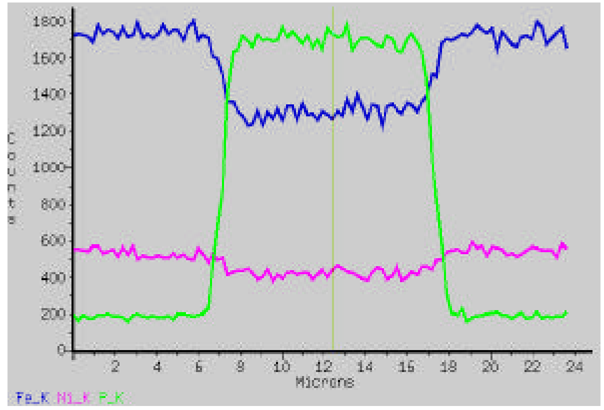

Fig. 2. *X-ray element profiles through the barringerite spindle in Fig.1 (white line).*

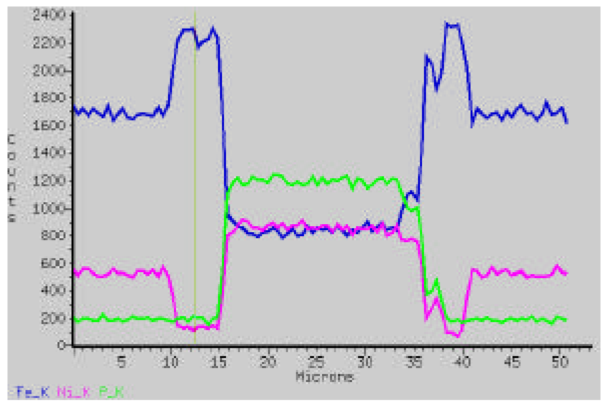

Fig. 3. *X-ray element profiles through a schreibersite plate. Note the swathing kamacite.*

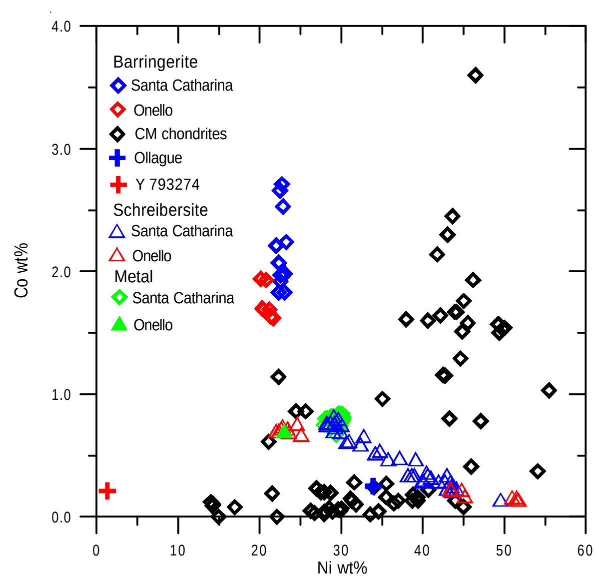

Fig. 4. *Co vs. Ni in barringerites, schreibersites and Fe,Ni metals. Our data are for Santa Catharina and CM chondrites. Other data are from [1,2,6].*