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# Barbianello: An ungrouped nickel-rich iron meteorite found in Italy

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**Abstract**–An unusual iron was found in 1960 in Barbianello (northern Italy, Pavia municipality) by a farmer, Clemente Allini, ploughing his fields. Years later, the iron was recognized as a meteorite but not officially classified. Our investigations indicate that Barbianello is a unique nickel-rich ataxite with dark and light regions texturally similar to, but compositionally distinct from, Santa Catharina iron. The light regions are chemically homogeneous, have a Ni content of 27.1 wt%, and a composition similar to irons of group IAB-IIICD. The dark regions are inhomogeneous with Ni ranging from 40 to 58 wt% and oxygen up to 20 wt%. Relics of unoxidized metal and textural relationships indicate that, unlike Santa Catharina, the dark regions result from the oxidation of a metal compositionally distinct from that of light regions.

## INTRODUCTION

On a mid-October day in 1960 (or 1961) at approximately 3 p.m., a farmer named Clemente Allini from Redavalle was ploughing a corn field in the locality Antoniana Piccola in the Barbianello municipality (Pavia; 45°03′28″N 9°11′44″E) following a bustrophedic path. Walking behind his oxen, he saw a "black heavy stone with metallic luster" lying on the surface of a new furrow aside.

Clemente Allini brought his find home claiming that it was a fallen meteorite, but when he showed it to a teacher of the local school, he was told that the object was a slag. Allini was disappointed but not fully persuaded. Taking advantage of the intrinsic physical properties of his find, Allini regarded the object as a useful weight, and assigned it to the not very flattering function of being the doorstopper of his cowshed.

Clemente Allini kept referring to the weight as "the meteorite," and in 1972 a curious relative of his, the young Carla Allini, decided to give the object another look. She brought it to her teacher Enrico Affini who, aware of being unqualified as meteoriticist, submitted the sample to the experience of Giuseppe Giuseppetti, professor of mineralogy at the University of Pavia. Based upon a visual examination and preliminary bulk analyses carried out in 1974 (using atomic absorption spectroscopy [AAS] and traditional wet methods), the doorstopper was eventually identified as an unusually Ni-rich iron meteorite.

Clemente Allini donated the meteorite to the Municipal Natural History Museum of Milano, Italy, where its main mass (479 g) is now preserved (Inventory number: MSNM-M-31767).

## EXPERIMENTAL TECHNIQUES

Major and trace elements abundances of Barbianello were determined by INAA at the Max-Planck-Institut für Chemie (Mainz) on a 86.65 mg chip, sampled from a light zone of the iron (see discussion in the Petrographic and Chemical Characters section) apparently devoid of alteration. Following irradiation in the TRIGA MARK II reactor (University of Mainz, Kernchemie), the sample was repeatedly counted on large Ge(Li) detectors. Peak deconvolution of spectra utilize procedures described in Kruse (1979). Table 1 shows the unpublished data of three distinct individuals of the large hexaedrite North Chile, analyzed during the last 30 years in our institute (kindly provided by B. Spettel). There is good agreement between our results and those given by Kracher et al. (1980). The results of Barbianello were obtained by the same procedures and are shown in Table 2.

WDS Electron microprobe analyses were obtained on a mounted polished chip of iron at CNR Istituto di Geoscienze e Georisorse, Padova, with a Cameca Camebax operating at 15 kV and 15 nA. The results of these analyses are shown in Table 3.

Backscattered electron images were taken using a Philips

Table 1. INAA of individual North Chile irons (Hexaedrite) as analyzed in Max-Planck-Institute für Chemie, Mainz (MPI) and literature data.

| | San Martin MPI | σ (%) | Filomena MPI | σ (%) | Tocopila MPI | σ (%) | Tocopila Kracher et al. (1980) |
|---|---|---|---|---|---|---|---|
| Fe% | 94.12 | 3 | 93.9 | 3 | 91.8 | 3 | – |
| Ni% | 5.82 | 4 | 6.02 | 4 | 5.60 | 5 | 5.54 |
| Cr ppm | 43 | 15 | 85 | 7 | 80 | 15 | – |
| Co ppm | 4390 | 3 | 4360 | 3 | 4710 | 4 | 4400 |
| Ga ppm | 63.4 | 3 | 66.5 | 4 | 60 | 5 | 58.6 |
| Ge ppm | 154 | 10 | 188 | 10 | 172 | 10 | 176 |
| Ir ppm | 3.68 | 3 | 3.96 | 3 | 3.95 | 4 | 3.5 |
| Cu ppm | 128 | 10 | 132 | 10 | 128 | 5 | 135 |
| As ppm | 4.53 | 3 | 9.02 | 4 | 3.94 | 5 | 4.6 |
| Pt ppm | 25.1 | 5 | 29 | 5 | 24 | 7 | – |
| Os ppm | 1.5 | 15 | 1.42 | 7 | – | – | – |
| Au ppm | 0.568 | 3 | 0.636 | 3 | 0.562 | 3 | 0.63 |
| Mo ppm | 7.9 | 10 | 7.85 | 7 | – | – | – |
| Ru ppm | 20.6 | 12 | 21.3 | 9 | – | – | – |
| Pd ppm | 2.8 | 15 | 2.4 | 10 | – | – | – |
| W ppb | 2570 | 3 | 2710 | 5 | 2860 | 5 | 2600 |
| Re ppb | 219 | 7 | 250 | 10 | 230 | 15 | 200 |

Table 2. Bulk chemical analyses of Barbianello (INAA).

| | | σ (%) |
|---|---|---|
| Ni% | 27.1 | 4 |
| Co ppm | 5480 | 3 |
| Ga ppm | 28 | 5 |
| Ge ppm | 73 | 25 |
| Ir ppm | 1.51 | 3 |
| Cu ppm | 1380 | 4 |
| As ppm | 16.6 | 3 |
| Pt ppm | 1.6 | 30 |
| Os ppm | 1.4 | 10 |
| Au ppm | 1.390 | 3 |
| Sb ppb | 770 | 10 |
| W ppb | 220 | 20 |
| Re ppb | 76 | 20 |

Table 3. Mean composition of Barbianello's mineral phases (oxide wt%).

| | Schreibersite | | Kamacite | | Taenite | | $Ni_3Fe$[b] | FeNi ox[b] | Akag |
|---|---|---|---|---|---|---|---|---|---|
| #[a] | 14 | | 9 | | 19 | | 1 | 1 | 4 |
| | mean | σ (%) | mean | σ (%) | mean | σ (%) | | | |
| P | 14.92 | 0.2 | bdl[c] | – | bdl | – | bdl | bdl | bdl |
| S | 0.02 | 0.02 | 0.04 | 0.01 | 0.03 | 0.01 | 0.19 | 0.39 | 0.06 |
| Cl | 0.03 | 0.06 | bdl | – | bdl | – | 0.04 | – | 4.47 |
| Cr | 0.02 | 0.03 | bdl | – | bdl | – | bdl | – | bdl |
| Fe | 34.99 | 0.9 | 93.37 | 0.56 | 71.55 | 1.16 | 33.45 | 42.59 | 53.26 |
| Co | 0.06 | 0.03 | 0.92 | 0.1 | 0.58 | 0.05 | 1.24 | 0.51 | 0.44 |
| Ni | 49.87 | 0.84 | 5.37 | 0.67 | 27.73 | 1.03 | 63.41 | 43.57 | 0.63 |
| Sum | 99.91 | – | 99.71 | – | 99.27 | – | 98.33 | 87.06 | 58.88 |

[a]The # row indicates the number of electron microprobe analyses. For $Ni_3Fe$ and oxidized FeNi only representative analyses are reported.
[b]The low total of $Ni_3Fe$ and FeNi oxide (ox) reflects oxidation of metal.
[c]bdl = below detection limit.

XL40 scanning electron microscope (SEM) at CNR Istituto di Chimica e Tecnologie Inorganiche e dei Materiali Avanzati in Padova.

Etching was performed on a polished section spreading a solution of 5% nitric acid in alcohol (Nital) on the surface for about 10 min. Afterward, the sample was carefully washed under a stream of deionised water and heated to 150 °C.

## PETROGRAPHIC AND CHEMICAL CHARACTERS

The original mass of the iron was 860 g. After it was found, no precautions were taken to preserve it from oxidation. The iron now appears severely altered on the surface, but still preserved inside (Fig. 1). Etching on a polished surface did not reveal macroscopic Widmanstätten patterns, which are consistent with the high Ni content of this meteorite.

Mineralogic study on a polished section revealed that even fresh polished surfaces show irregular brownish areas of staining and corrosion. SEM backscattered electron imagery (BEI) shows that Barbianello is composed of light and irregular dark regions (Fig. 2), the last of which corresponds to the stained areas observed in reflected light.

In the light regions, iron is homogeneous and consists almost entirely of taenite (Ni ~27 wt%, EDS analyses) with minor plates of kamacite and schreibersite. Kamacite is found in isolated, irregular, subrounded pods or around grains and shafts of early-crystallized schreibersite (Fig. 3). Bright, up to 5 μm-wide, bands locally cross-cut the light regions. EDS analyses on these bands and on the surrounding metal is unable to point out any significant compositional difference. The dark areas are inhomogeneous, show variable Ni contents, and typically contain oxygen (EDS analyses). Relationships between dark and light regions are illustrated in Figs. 2 and 4, where the alteration pattern of dark regions is also evident. The dark regions are often crosscut by a regular network of three series of parallel lines that can be either lighter or darker than their host (Fig. 4). Lines in adjacent dark regions are identically orientated, even when they are separated by unaltered metal (Fig. 4). It is also observed that the width of darker lines increases at the intersection of two such lines. The occasional presence of relics of unaltered, high Ni (~63 wt%) metal, where alteration appears to propagate along these sub-parallel lines (Fig. 5), provides evidence that darker lines might represent traces of cleavage along which oxidation developed first. Variable oxygen contents (EDS) were consistently obtained along alteration path of these lines. A complementary hypothesis to account for the presence, and occasional coexistence, of brighter lines is that the last one represents lamellae with distinct composition possibly exolved along the cleavage of the host phase. Lighter lines are too thin to allow representative analysis.

The search for troilite, graphite or silicate mineral, carried out on two distinct polished mounts with both optical and electron microscope was negative in both light and dark areas.

Electron microprobe analyses (EMPA) carried out on mineral phases are reported in Table 2. Due to technical

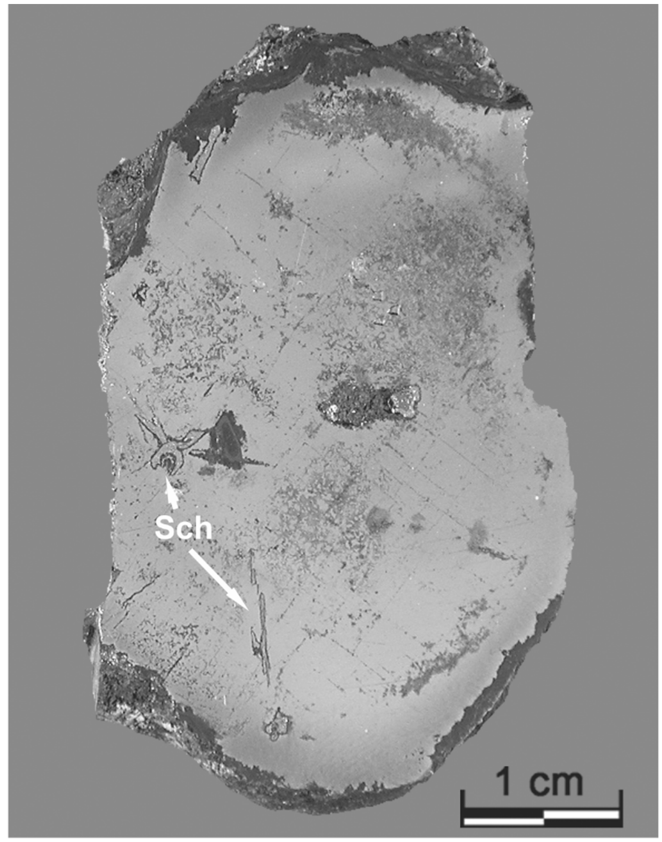


Fig. 1. Polished surface of a chip of the Barbianello iron meteorite. Alteration on the newly polished surface, corresponding to the dark regions, is evident. White arrows indicate schreibersite crystals (photograph by Stefano Castelli [2001]).

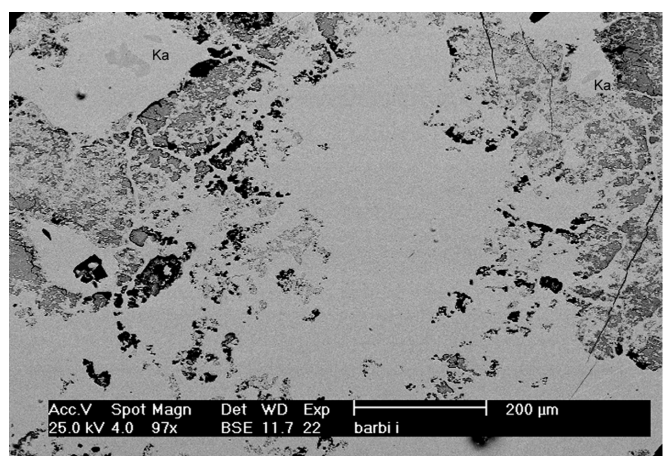


Fig. 2. Backscattered electron image of the Barbianello iron meteorite with light and dark regions arranged in a sort of geometrical pattern. Kamacite (Ka) is only present within the light regions.

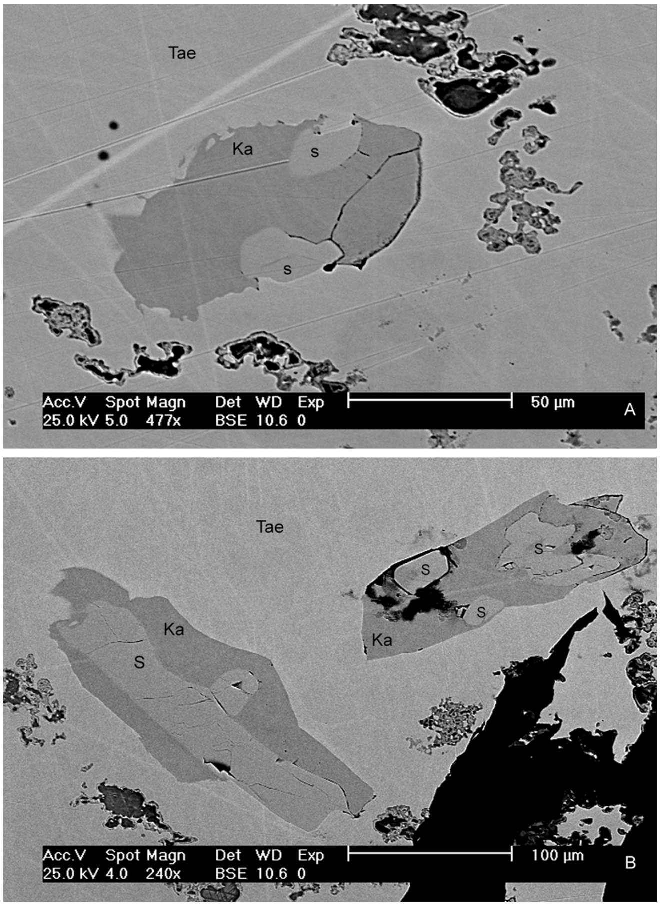


Fig. 3. Backscattered electron image of the Barbianello iron meteorite. Kamacite (Ka) is found in isolated irregular, subrounded pods or around grains and shafts of early-crystallized schreibersite (S). Taenite (Tae) represent the main component. The irregular dark areas surrounding black zones (holes and fractures) represent domains of alteration.

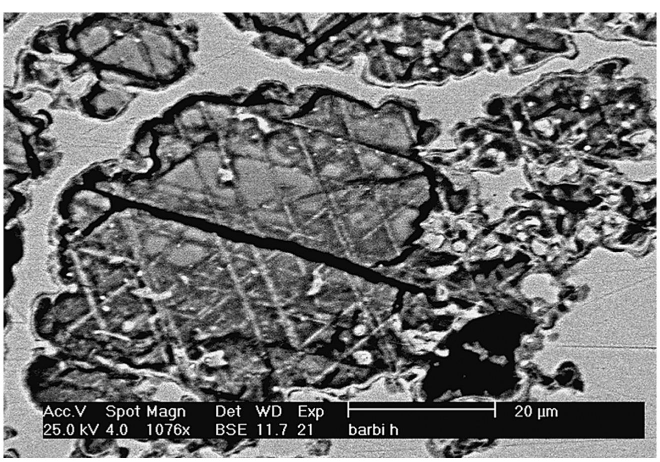


Fig. 4. Detail of dark region showing three regular sets of intersecting lines. Lines can be either darker or lighter than the host and likely mimic the cleavage structure of the original metal. Lighter lines might represent exolved lamellae of distinct composition.

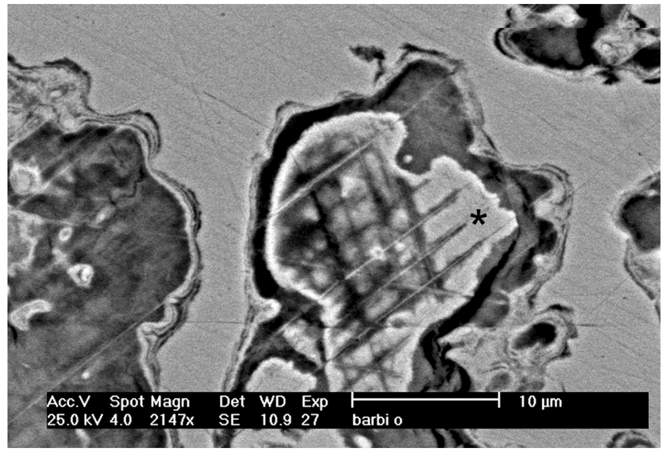


Fig. 5. Relics of metal with $Ni_3Fe$ composition within a dark area. The alteration appears to pervade the metal starting from the regular sets of line. The alteration is wider at the intersection of two lines. The continuation of these lines from one dark zone to the adjacent one suggests the structural iso-orientation of their host metal. Chemical composition of the point indicated with a star is Ni 63.41 wt%, Fe 33.45 wt% and Co ~1.2 wt%. The low total of this analysis (98.06 wt%) is due to the overlap of the EMP spot with the surrounding altered areas.

limitations of our instrument, O was not measured, however, EDS semi-quantitative analyses was used to check for the consistency between the low EMPA sum and the relative oxygen abundance. The Ni content of taenite in light regions ranges from 27.0 to 28.6 wt%. Kamacite as well as schreibersite, was only observed within light, relatively low-Ni, regions. The mean Ni value in kamacite is 5.37 and its mean Co content (0.92 wt%) is slightly higher than in taenite (0.58). Schreibersite, is homogeneous with P ≅ 14.9 wt% and low Co content (Fig. 6).

The chemical composition of dark regions is much less homogeneous. It ranges from Ni ≅ 40 wt%, Fe ≅ 40 wt%, with a sum of around 82 wt%; to Ni 58 wt%, Fe 37.6 wt% with a total of 96.3 wt%. Unaltered metal, found as relic within some dark regions (Fig. 5), has a composition of Ni 63.41 wt%, Fe 33.45 wt% and Co around 1.2 wt%. The low total (~98 wt%) of the analyses is due to the partial overlap of the EMP spot on the surrounding altered areas.

A mineral phase characterized by high Cl content (EDS) is also present (Table 3). This phase has a fairly constant total of 58.5 wt%, a mean Cl content of 4.5 wt% (range 3.4–6.1 wt%) and Ni ranging from less than 1% to 10%. The composition is similar to that of Akaganeite ((Fe[O, OH, Cl]). The presence of Cl-rich phases is common in iron meteorites and has been observed also in chondrites. They are secondary products responsible for the quick alteration observed in some meteorites, and for the dramatic collapse of some irons.

The high Ni content, determined by previous AAS analysis and by EMPA on light regions, could be confirmed by INAA (Table 2). The similarity between INAA and mean EMPA Ni contents, proves that the small chip selected for

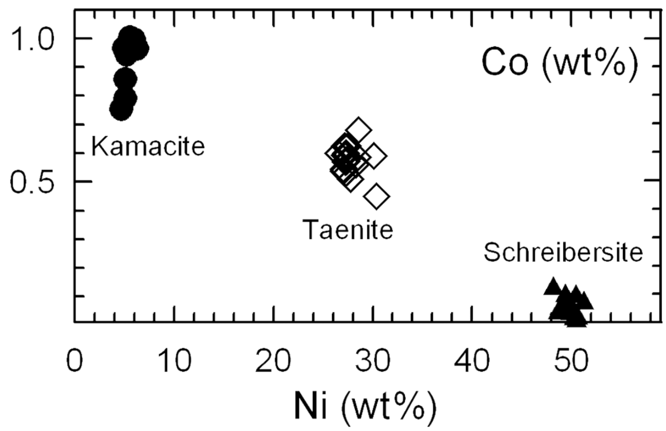


Fig. 6. Variation diagram of Co versus Ni in the main mineral phases of the Barbianello iron meteorite shows a good negative correlation.

bulk chemical analysis was actually sampled from, and is, therefore, representative of the fresh, unoxidized iron that is typical of light regions. Moreover, as AAS, EMPA, and INAA were performed on different unaltered samples of the meteorite, their similar Ni content indicates that the composition of metal, in the light regions, is homogeneous. No bulk analysis was carried out on the oxidized, altered iron. Siderophile trace elements indicate that the analyzed iron bears chemical similarities to IAB-IIICD irons (Fig. 7). Based on its Ge/Ga ratio, as defined by Choi et al. (1995), its composition falls in the IAB-IIICD range. Concentrations of Ga (28 ppm) and Ge (73 ppm) are higher than in typical IAB-IIICDs, yet comparable to concentrations in the Ni-rich IABs San Cristobal and Yamato (Y-791694; "Y-79") as well as the ungrouped iron Elephant Moraine (EET 87506; "ET87"). The high Cu concentration of 1380 ppm also falls well in the range of IAB-IIICD irons and is comparable to concentration in Santa Catharina (SanCat) and Twin City (TwC). Ir in Barbianello follows the trend depicted by EET87, San Cristobal, Y79, and Oktibbeha Count. However, the distinctly lower than IAB-IIICD As (16.6 ppm) and Au (1.39 ppm) contents allow us to classify this iron as chemically ungrouped. Au, As, Co, and Sb contents are all above the main threshold values indicated by Wasson and Kallemeyn (2002) as distinctive of iron-meteorites with compositional links to the IAB clan, however, Barbianello does not fit within any of the IAB group or subgroup.

## DISCUSSION

Barbianello meteorite is characterized by the presence of distinct dark and light regions similar to those described in high-Ni Santa Catharina iron meteorite, namely in sample USNM #3043 (Zhang et al. 1990). However, while their structures are remarkably similar, chemical composition of dark and light regions in Barbianello and Santa Catharina differ significantly. In Santa Catharina, light regions contain 35 wt% Ni and no detectable oxygen, while dark regions contain Ni 45–50 wt% and oxygen 7–12 wt%. In Barbianello, light regions contain Ni 27.7 wt%, a chemical composition that is similar to the lower-Ni Santa Catharina (e.g., sample USNM #6293; Zhang et al. 1990), and dark regions contain Ni 40–58 wt% with a sum of measured major elements ranging from 79 to 96 wt%. If all the missing element were oxygen (not measured by EMPA, but semi-quantified by EDS analyses) it would range between 21 and 4 wt%. It is worth noting that Cl is never a major component in the dark, high-Ni regions. Moreoever, the detected Cl-rich phase, possibly akaganeite, has very low Ni. Barbianello dark regions also contain relics (Fig. 5) of a primary, unaltered Ni-rich phase (Ni 63.5 wt%) with a Fe/Ni ratio of 0.52 and a composition corresponding to that of awaruite ($Ni_3Fe$). The variation of Ni and Fe/Ni ratio versus oxidation is reported in Fig. 8 for both light and dark regions. While light regions are remarkably homogeneous, dark regions depict continuous negative trend of Ni, and positive trend of Fe/Ni, versus increasing oxidation. Both trends start from the composition of the metal relicts observed within the dark regions (Fig. 5). This correlation, coupled with textural evidence, suggests that the observed trends derive by increasing oxidation of a primary phase having the composition of the relic metal actually found within the dark regions.

## CONCLUSIONS

The high Ni composition of the investigated iron left the first scientist who recognized its extraterrestrial nature with some legitimate open questions. Iron meteorites with Ni contents higher than 25 wt% are, in fact, few in number. New mineralogical and chemical data indicate that this meteorite, although similar to IAB-IIICDs, is actually unique, and is classified as an ungrouped ataxite.

Barbianello meteorite shows a dark- and light-regions structure similar to that of the high Ni (35 wt%) Santa Catharina. Light regions in Barbianello are homogeneous and unaltered and have a bulk composition (~27 wt% Ni by INAA) similar to the homogeneous low Ni Santa Catharina iron (Ni 28.2 wt%). Light regions in Barbianello are mainly composed of taenite (Ni 27 wt%) with quantitatively subordinate kamacite (Ni 5.4 wt%), often nucleated around schreibersite. Dark regions are inhomogeneous with Ni 40–58 wt% and up to 20% oxygen (calculated). The dark regions show compositional trends and textural relationships indicating that, unlike in Santa Catharina, dark regions do not simply represent secondary structures formed by terrestrial alteration superimposed to the light regions (Zhang et al. 1990), but light and dark regions have significant, primary, bulk compositional differences.

The presence of Cl-rich phases indicates a long residence time in the ground (Buchwald and Clarke 1989), we therefore assigned Barbianello to the group of meteorite finds. The

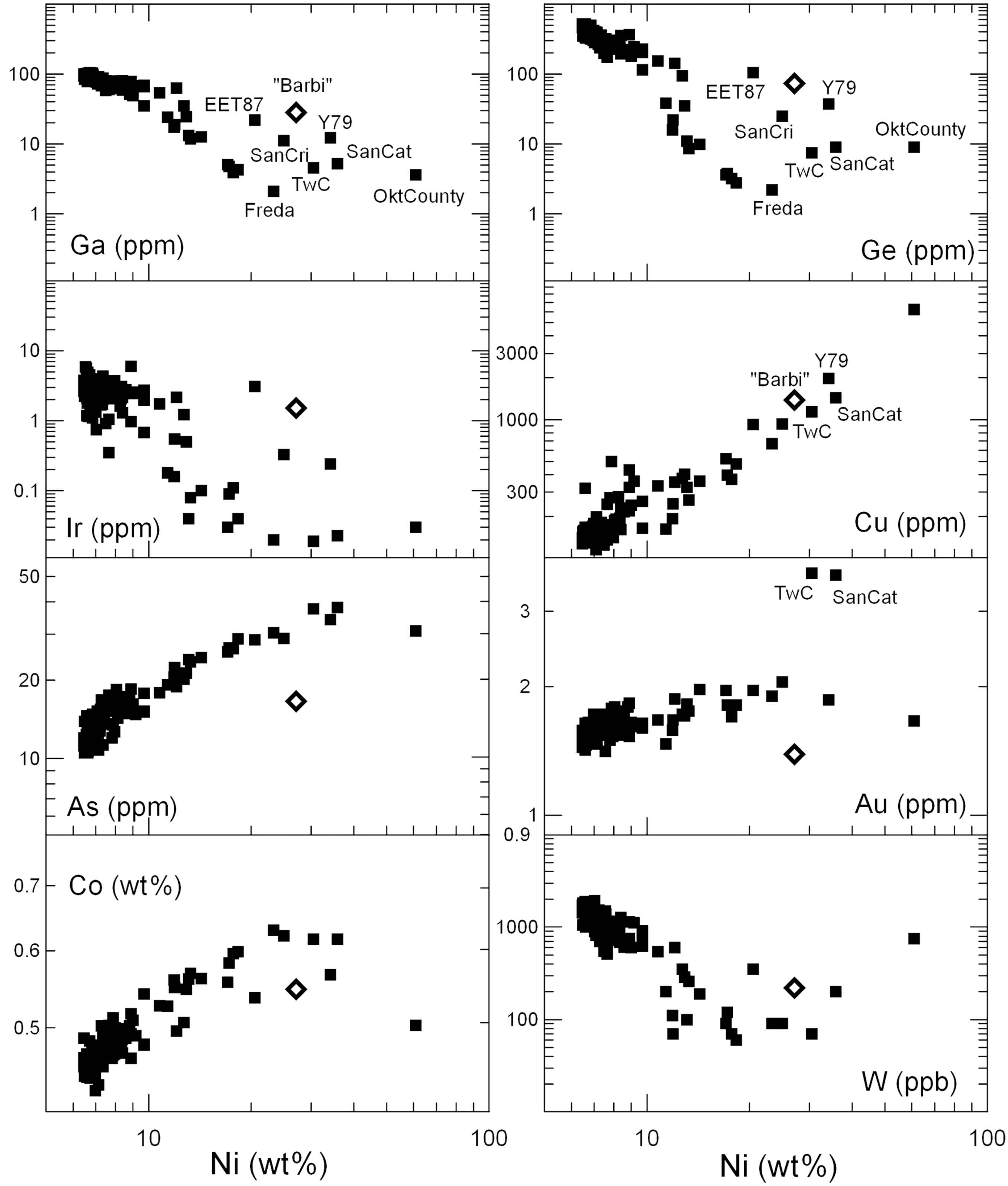


Fig. 7. Trace element composition of the new ungrouped iron Barbianello ("Barbi" open diamond) compared to IAB-IIICD irons (black squares). The ungrouped iron Elephant Moraine (EET 87506; "EET87") and the Ni-rich IABs San Cristobal (SanCri), Yamato (Y-791694; "Y79"), Oktibbeha County (OktCounty), Santa Catharina (SanCat), Twin City (TwC) and Freda are indicated for comparison. Data of IAB-IIICD irons are taken from Choi et al. (1995) and Wasson and Kallemeyn (2002).

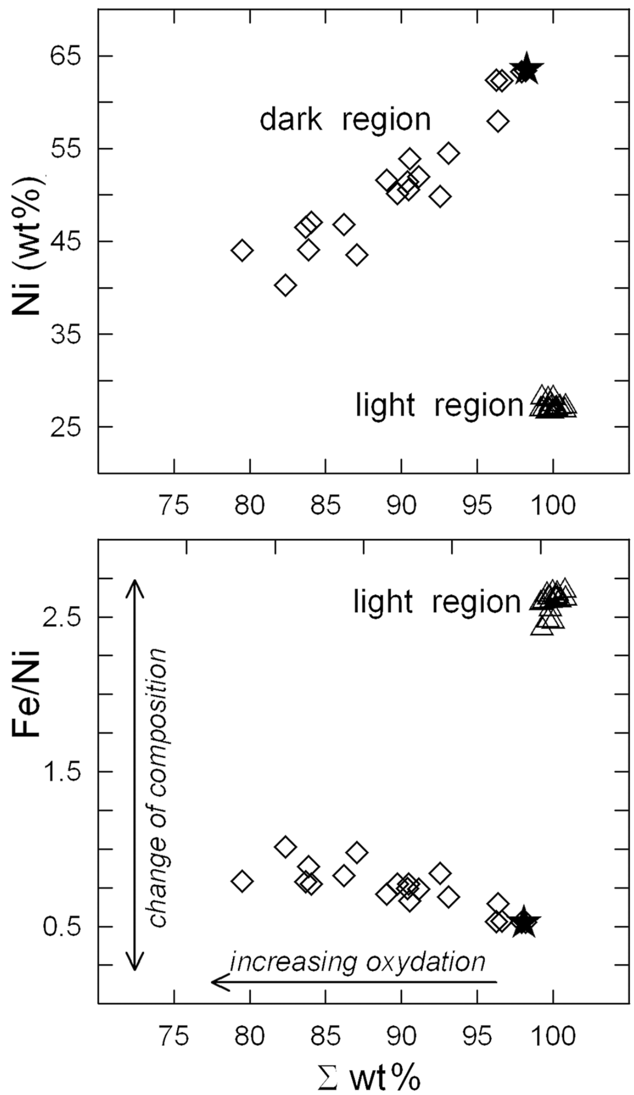


Fig. 8. Variation diagram of Ni (a) and Fe/Ni (b) versus the sum of elements measured at the EMPA (Fe, Ni, Co, S, Cl, P, Cr) for taenite, Ni-rich metal relics and different points within the dark regions. Since EDS analyses show that O is the only (above detection limit) missing element, we argue that the sum of elements is an indirect index of the oxidation. The light regions are homogeneous (full triangles). The dark regions (diamonds) depict continuous trends of decreasing Ni and slightly increasing Fe/Ni with increasing oxidation. Metal relics observed within the dark region (star) represent the Ni-rich end member of both trends.

presence of Cl-rich phases warns particular care must be taken in the storage of Barbianello to preserve it from alteration and collapse. Rust must be removed from the iron before washing it with anhydrous alcohol and heating it to evaporate residual water. After the iron is cleaned and dried, we recommend keeping it dry in a desiccated container.

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*Editorial Handling*—Dr. Edward Scott

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