Journal of Archaeological Science xxx (2017) 1–7

Contents lists available at ScienceDirect

Journal of Archaeological Science

journal homepage: http://www.elsevier.com/locate/jas

Bronze Age iron: Meteoritic or not? A chemical strategy.

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ARTICLE INFO

Article history:
Received 12 January 2017
Received in revised form
5 September 2017
Accepted 7 September 2017
Available online xxx

Keywords:
Iron
Bronze age
Iron age
Meteorite
Iron ore

ABSTRACT

Bronze Age iron artifacts could be derived from either meteoritic (extraterrestrial) or smelted (terrestrial) iron. This unresolved question is the subject of a controversy: are some, all or none made of smelted iron? In the present paper we propose a geochemical approach, which permits us to differentiate terrestrial from extraterrestrial irons. Instead of evaluating the Ni abundance alone (or the Ni to Fe ratio) we consider the relationship between Fe, Co and Ni abundances and their ratios. The study of meteoritic irons, Bronze Age iron artifacts and ancient terrestrial irons permit us to validate this chemical approach. The major interest is that non-invasive *p*-XRF analyses provide reliable Fe:Co:Ni abundances, without the need to remove a sample; they can be performed in situ, in the museums where the artifacts are preserved. The few iron objects from the Bronze Age *sensu stricto* that could be analyzed are definitely made of meteoritic iron, suggesting that speculations about precocious smelting during the Bronze Age should be revised. In a Fe:Co:Ni array the trend exhibited by meteoritic irons departs unambiguously from modern irons and iron ores. The trend of Ni/Fe vs Ni/Co in different analysis points of a single object corroded to variable extents provides a robust criterion for identifying the presence of meteoritic iron. It opens the possibility of tracking when and where the first smelting operations happened, the threshold of a new era. It emphasizes the importance of analytical methods for properly studying the evolution of the use of metals and metal working technologies in our past cultures.

1. Introduction

Paradoxically, a number of iron artifacts from the Bronze Age have been found in a variety of Old World culture areas (e.g. Li Chung, 1979; Waldbaum, 1980, 1999; references therein; Yalçın, 1999; Jean, 2001) with the recurrent question about the origin of the iron: extraterrestrial (meteoritic) or terrestrial (smelted)? "Bronze Age Iron" means iron that appears within Old World culture areas, prior to the advent of iron smelting on some scale in those areas.

The two possibilities are supported by a number of valuable arguments which are summarized as follows: Nickel (Ni) is the signature element for meteoritic iron. The Ni content is sometimes too low to be meteoritic which could be explained either by the use of Ni rich iron ores (Ni poor relative to meteorites) or by weathering with preferential loss of Ni. The confusion is increased by some conflicting results on the same artifacts by different methods at different times, with the difficulty that metallographic analyses which could solve this contention are impossible on such rare and fragile objects (*On Line* Supplementary Material: A1 *Meteoritic vs. Terrestrial Iron: a controversy*).

In this work we examine a new geochemical approach involving the analysis of three elements (Fe:Co:Ni) instead of two (Fe:Ni) with the aim of differentiating between the above mentioned possibilities. This is enabled by the recent development of high performance portable XRF analyzers (*see On Line* Supplementary Material: A2 *Analytical methods*). Our argument proceeds as follows:

- Consider a data set of meteoritic irons, including oxidized specimens.
- Analyze irons of diverse ages: Bronze Age, Bronze to Iron Age transition and Iron Age, and take benefit of recent high quality analyses (*see On Line* Supplementary Material A3. *Samples*).
- Iron ore compositions are also considered. Lateritic alteration products derived from peridotitic rocks are common from Croatia to Greece, Turkey, Iran, Cyprus … These may be valuable iron ores and contain significant amounts of Co and Ni unlike

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http://dx.doi.org/10.1016/j.jas.2017.09.008
0305-4403/

sedimentary iron ores which are more common in western Europe (*see On Line* Supplementary Material: A3.6. *Iron ores*). Since Brun *in* Schaeffer (1939) suggested that the 13th century BCE Ugarit (Syria) iron axe could be derived from iron sulfide ore (pyrrhotite $Fe_{1-x}S$; x = 0 to 0.2), such material will be considered in this study using data from the literature (Bamba, 1985).

2. Results

2.1. Iron meteorites

The analytical results for polished surfaces of iron meteorites, outer oxidized surfaces of iron meteorites *(OLSM* Table A1*)* and literature compositions for different classes of iron meteorites are presented in Fig. 1, in addition to a compilation of iron meteorite compositions from the meteoritical bulletin database (http://www.lpi.usra.edu/meteor/): 176 meteorites classified from 1986 to 2016 (*OLSM*, Table A2). The variations within this population are best illustrated in a Ni/Fe vs Ni/Co diagram (Fig. 1)

Fresh meteorites exhibit a Ni/Fe range from 0.058 to 0.40 (average 0.102) whereas oxidized/weathered surfaces of iron meteorites exhibit lower values down to 0.009. We checked that the variations observed are not due to the variability within one single meteorite as illustrated by the results for Morasko meteorite which we could analyze in 31 points, hence assessing the internal variability of its Co and Ni content, and the different compositions of fresh and weathered surface. The results obtained for fresh metal surfaces is within the range of those reported in the literature (NAA analysis of large samples, Pilski et al., 2013) with restricted standard deviations smaller than the variability range observed for the whole data set (*On line* Supplementary Material; A3.2 *Iron meteorites)*

Surfaces oxidized during the atmospheric flight exhibit similar ratios. The case is different for finds, which have been weathered. This indicates that during weathering, a surficial layer is impoverished in Ni relative to Fe whence the Ni/Fe ratio cannot be used as a reliable indicator of the meteorite type for weathered samples. A comparable variation is observed for the Ni/Co ratio. Notice that the chemical properties relative to weathering are in the order Fe > Co > Ni, whence the positive correlation between Ni/Fe and Ni/Co as will be better illustrated in the following subsection for the case of the Ugarit axe, analyzed in different spot analyses (Fig. 2). It follows that the Ni/Fe ratio alone cannot be used as an indicator of the source of iron.

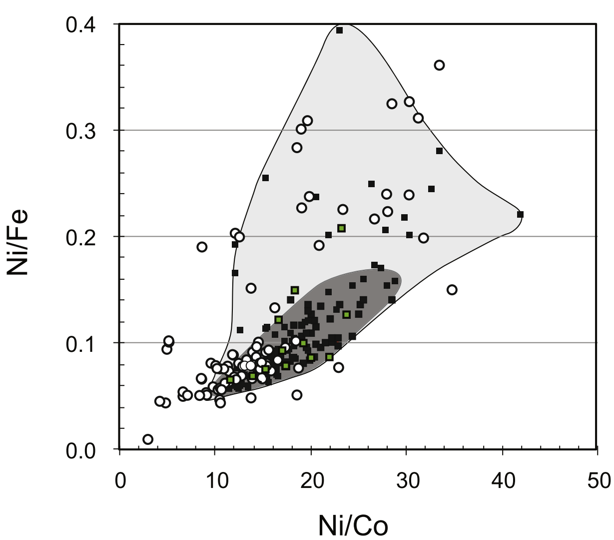

Fig. 1. Ni/Fe vs Ni/Co in iron meteorites. Black squares and gray area are from literature data for fresh iron meteorites (http://www.lpi.usra.edu/meteor/). Green squares: average compositions of the major iron meteorite groups (Mittlefehldt et al., 1998). White circles: *p*-XRF analyses of both polished and oxidized outer surface (this work). P-XRF measurements on fresh surfaces are similar to literature data. On the average, oxidized compositions extend to slightly lower Ni/Co and Ni/Fe ratios. 80% of the data for fresh meteorites are enclosed in the high-density field (dark gray). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

2.2. Bronze Age archaeological artifacts

Analytical results are listed in the *on line supplementary material,* Table A4 with references to where a description can be found. Additional information can be found in OLSM section A4.1.

2.2.1. *Ugarit axe* (*Syria 1400 BCE*)

We performed ten spot analyses at different places on both sides of the blade (see Jambon et al., 2017). The Ni concentrations of 1.7 up to 7.6% Ni (calculated on an oxygen free basis) document nicely the effect of weathering. The high Ni contents are undoubtedly the signature of meteoritic iron whereas the lowest values correspond to pervasively oxidized spots. These differences probably result from rust flakes detachment from the surface. The variations of Ni/Co and Ni/Fe correlate fairly well with Ni content, which can be viewed as an index of weathering, as displayed in Fig. 2.

The Ni/Fe and Ni/Co ratios plot on the trend defined previously for iron meteorites, Fig. 3, which is interpreted as corresponding to different degrees of weathering. Our results for the Ugarit axe show both higher and lower Fe/Ni ratios compared to the analysis reported in Schaeffer (1939). The sampling made by Schaeffer being undocumented, we assume that it was a surface chip, an average of more and less oxidized material, but no obvious mark of sampling is presently visible on the axe blade.

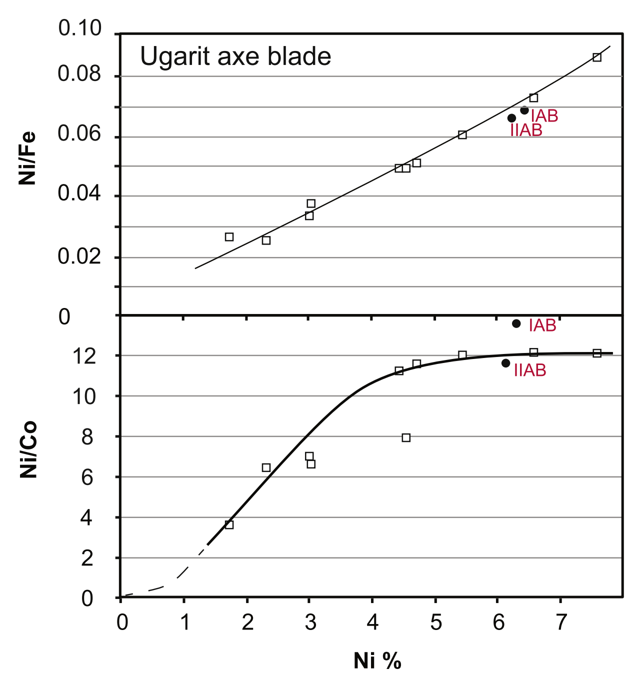

Fig. 2. Plot of Ni/Fe and Ni/Co against Ni abundance for Ugarit Axe. The steady variation of the Ni/Fe ratio against Ni indicates that Ni is preferentially leached during weathering whereas, Fe oxidized to Fe^{3+} is not. The Ni/Co ratio remains constant for mild weathering and then decreases when part of Co is oxidized to Co^{3+}. Average composition of IAB and IIAB meteorites are plotted for reference.

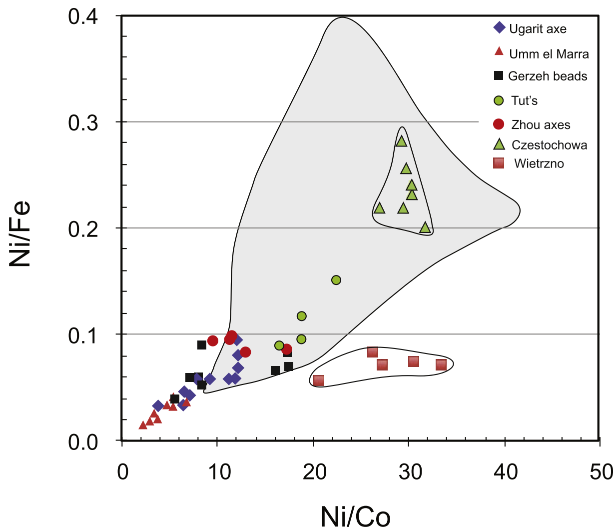

Fig. 3. Same as Fig. 1 for Bronze Age and Iron Age iron artifacts. The gray area is taken as a reference from Fig. 1. Most compositions are clearly displaced to lower Ni/Co and Ni/Fe values. Well documented specimens like Umm el Marra pendant and Ugarit axe exhibit a clear positive correlation corresponding to variable extents of weathering, undistinguishable from the bulk trend. Tut's dagger and Gerzeh beads, which have been demonstrated to be of meteoritic origin fall on the same correlation. This work, except Tut's, Alaça Höyük and Zhou axes data taken from the literature. Notice the apparent out-of place field for Wiertzno axe.

2.2.2. Other Bronze Age artifacts

The results for the Gerzeh beads (Egypt; 3200 BCE), Umm el Marra pendant (Syria; 2300 BCE), Tut's dagger, bracelet and head-rest (Egypt; 1350 BCE), Shang Dynasty axes (China; 1400 BCE) and Alaca Höyük dagger, (Turkey; 2500 BCE) are commented in detail in the *On line* supplementary Material; A4.1. The only specimen for which one single analysis is available is Tut's dagger the meteoritic origin of which is beyond any doubt (Comelli et al., 2016; Ströbele et al., 2016). For all other specimens we have 2 to 9 analytical points. Both Co and Ni are highly variable (0.8–8.5% Ni) but in the Ni/Fe vs. Ni/Co plot, Fig. 3, the data points fall nicely on the same trend as Ugarit axe data. For some of the artifacts the highest Ni concentrations are in the range of meteoritic values (e.g. Gerzeh beads, Alaca Höyük dagger, Tut's jewelry) while some data points fall below 3.5% Ni. Taken at face value and if the conservative threshold of 5% Ni were considered (e.g. Yalçın, 1999), one would infer the presence of both terrestrial and meteoritic iron in one and the same sample!

In the present interpretation however, replicate analyses including Co analyzes, indicate that all artifacts tested are made of meteoritic iron. For the other artifacts (e.g. Umm el Marra pendant, Shang axe) the low Ni concentrations cannot therefore be considered as a proof of being terrestrial. The data points falling on the same correlation as meteoritic artifacts strongly suggests that they are meteoritic as well. In other words, the Ni/Fe ratio alone is not appropriate to conclude whether an artifact is made of meteoritic iron or not, or may be the threshold should be dramatically decreased. This indicates that the weathered surface exhibits variable Ni/Fe and Ni/Co. The trend for artifacts is similar to that observed for weathered meteorites with lower Ni/Fe and Ni/Co on the average. This is not surprising since the meteorites analyzed were only marginally weathered. To summarize, the range in both Ni/Fe and Ni/Co for meteorites and iron artifacts overlap, with a significant variability in Ni/Fe and possibly low Ni contents (down to less than 1%). According to the present observations, none of the Ni bearing iron artifacts, with low Ni content, was proved to be made of terrestrial iron.

Our preliminary conclusions may therefore read:

1) All results, the present *p*-XRF analyses and literature results as well, illustrate than one single object may exhibit various Ni contents depending on the analytical spot. This is not due to primordial metal heterogeneity but rather to a variable extent of weathering (corrosion). Most of us will agree that contents exceeding 5% Ni should be considered as meteoritic; the lower Ni contents from the same objects, especially when analyzed with the same technique, must be considered meteoritic as well.
2) When the Co results are considered, even though the Ni data alone could appear inconclusive, the Fe:Co:Ni correlation falls on one and the same trend with iron meteorites. Weathering is an important factor of variation in the Ni content. One way of accounting for this effect is to consider the Fe:Ni:Co correlations.
3) No nickel-poor iron from the Bronze age can be proved not to be meteoritic.
4) No nickel-rich iron object of the Bronze Age consists of smelted iron. We therefore may ask whether one single iron object from this time is not made of meteoritic iron, since the low level or even absence of Ni can no more be considered as a proof for the smelting origin of iron.
5) If our interpretation that the three iron objects from Tut's treasure are made of three different iron meteorites, is correct, this suggests an active search about iron meteorites.

2.3. Transition artifacts

Results are listed in OLSM Table A5. Complementary information is given in the OLSM A5.1.

2.3.1. Le louvre specimens

For both the halberd and the adze (Luristan, ca. 1300- 650 BCE), the Ni falls below the detection limit, while Co is above it (detection limit is 0.02%) which indicates a Co/Ni ratio > 10 and a Ni/Fe ratio < 0.005. Both artifacts are without ambiguity made of terrestrial iron. Casting a bronze socket indicates that the ability at smithing was not well mastered for these objets, which may be considered as benchmarks in bloomery iron smithing.

2.3.2. Zhou dynasty axes

The objects from early Zhou (about 1000 BCE) were first investigated by Foshag (in Gettens et al., 1971) who detected no nickel and concluded that the iron was not meteoritic. Gettens et al. however made insightful analyses, including microprobe analyses and metallographic examinations. They showed unambiguously that both artifacts are made from meteoritic iron. What interests us more are the chemical analyses of both metal and oxidation products, which fall within the field of iron meteorites (Fig. 3 and Table A4).

2.3.3. Neuchatel artifacts

Three needles, two nails and one hook were analyzed. Despite their chemical composition, the needle typology is identical to and typical of Bronze Age needles of that area. In other words they were probably produced in the same region, between 950 and 850 BCE according to dendrochronological dating (Rychner, 1979; Rychner-Faraggi, 1993) in the Late Bronze Age of western Switzerland. Their composition is typical of smelted iron which indicates that Late Bronze Age in Europe is not equivalent (technologically speaking) to Near Eastern Final Bronze Age. We know that iron was smelted further east at the same time (possibly as early as 1200 BCE in SW Asia) and iron ingots may have been imported as precious metal to make jewelry.

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2.4. Iron age artifacts

The results are listed in the *On line supplementary material; Table A5.2 with complementary informations in section A4.3.*

2.4.1. Present study

The Marsal ingots (NE France) are quite fresh. From the archaeological context they are dated at about 700 ± 100 BCE. Their Ni and Co contents are exceedingly low, mostly below the detection limit of our equipment. When Co and Ni are detectable the Co/Ni ratio is observed to exceed unity in strong contrast with meteoritic iron (<0.2) and clearly outside of the trend defined by meteoritic material. In addition the amount of Cu is sometimes significant (up to 0.5% in one of six ingots) in contrast to the composition of meteoritic metal. The different chemical compositions among the various ingots analyzed suggest several provenances that cannot be specified for the moment. For such low Ni values it is more convenient to show the data in an Fe/Co vs. Ni plot with a log scale. The field for Marsal ingots falls unambiguously apart from the meteoritic compositions (Fig. 4).

Irons from Poland

Czestochowa-Rakowa bracelets are also dated from Hallstatt C (800-600 BCE). Our Ni results are in agreement with those of Kotowiecki (2004) 18.5 and 12.5% Ni for CrZ1 and CrZ2 respectively, to be compared to our values of 15.5–18.4 and 18.1–21.2% Ni, an unusually high Ni content. Piaskowski (1982) gives comparable results for Crz1 of 18.25% Ni, 0.58% Co and 12.4% Ni for CrZ2. These compositions fall nicely in the field of iron meteorites. The suggestion of previous workers (e.g. Photos, 1989) that such high Ni metal could be produced from terrestrial ores is not supported in the present case by the chemical composition.

Wietrzno Axe (Hallstatt unspecified) is a special case, which illustrates the potential of the method. The data points in Fig. 3 plot below the field of iron meteorites despite a high Ni content (5.5–7.6% Ni) typical of iron meteorites indicating that for its Ni/Co ratio, the Ni content should be higher (Fig. 3). One simple explanation is that its metal is a mixture of terrestrial iron (low Co, low Ni) with meteoritic iron similar to that used for the bracelets. Doing so the Ni/Co ratio remains unchanged (the contribution from terrestrial iron is negligible) whereas the Ni/Fe ratio is significantly decreased. This explanation is substantiated by the observation that the blade is made of five layers (two high in Ni and three devoid of Ni; Piaskowski, 1982), which cannot be resolved with the *p*-XRF analyzer. This unexpected result suggests that the similarity between meteoritic iron and smelted iron was recognized and that the use of meteoritic iron was still a viable practice. Because of the rarity of iron meteorites with such a high Ni content exceeding 15%, it is likely that the same meteorite was used for the bracelets and the axe.

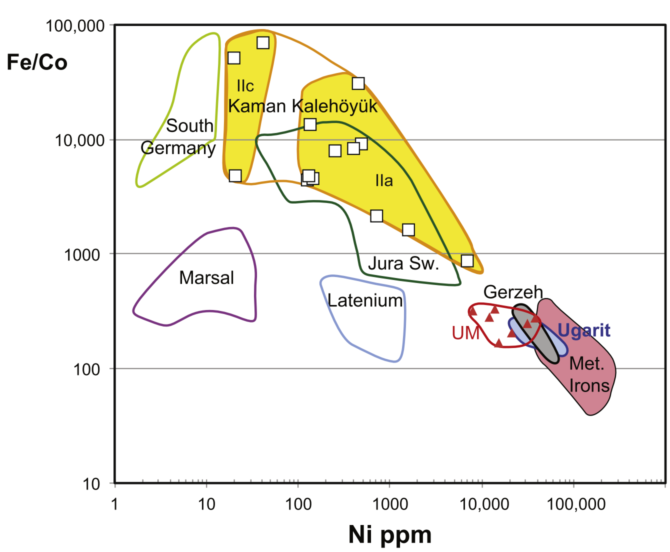

Fig. 4. Plot of Fe/Co against Ni for Bronze Age and Iron Age artifacts. The log scale permits to illustrate the variations for low Ni irons (e.g. smelted irons from sedimentary ores) and high Ni irons (e.g. meteoritic irons). At 1% Ni (10,000 ppm) the Fe/Co ratio permits to distinguish samples with otherwise similar Ni abundance. UM= Umm el Marra pendant (Syria) (Schwartz et al., 2003). Latenium = Neuchatel (Rychner, 1987). Jura Sw(itzerland) (Eschenlohr et al., 2007). White squares are data for Kaman Kalehöyük levels IIA and IIc (Turkey) from (Akanuma, 2006).

2.4.2. Literature data

We selected examples where archaeological artifacts were analyzed for Co and Ni on sufficiently well preserved samples (some metal is preserved): Fragments from Kaman Kalehöyük (Turkey) (Akanuma, 2006), Western European irons of Manching (South Germany) (Schwab et al., 2006) and two from Renningen and one from Grösseltal (South Germany) (Brauns et al., 2013). More information can be found in the *On line supplementary material; section A4.2.*

The results are plotted in Fig. 4. All data fields are presented in Fig. 4 and, as expected fall quite far from the meteoritic field.

Finally the more recent objects from Devélier-Courtetelle (Jura, Switzerland), a set of 67 objects, analyzed by Eschenlohr et al. (2007) are low in Ni (40–4000 ppm; average 1200 ppm) with a Co/Ni ratio ranging 0.02 to 3 (average 0.43).

2.5. Ni bearing iron ores

We showed that smelted and meteoritic irons can be distinguished from their Fe:Co:Ni composition, still according to previous suggestions we must investigate whether lateritic iron ores which reportedly contain some nickel, could produce iron distinguishable from meteoritic iron. As noticed by Pryce and Natapintu (2009) laterites cover a wide domain of compositions, but the ones we are concerned with are those developed on peridotites. These are rocks with dominant (>60%) olivine of formula $(Mg,Fe)_2SiO_4$. These contain significant amount of iron oxide (about 10% on the average) and little aluminum oxide (less that 3%).

2.5.1. Lateritic ores

The Fe, Co and Ni contents were measured across alteration profiles, from the fresh mother rocks to the iron oxide cap. The iron content increases from bottom to top, while the Ni first increases then decreases at the top where the iron ore is of the best quality (low silica content). The Ni/Fe and Ni/Co ratios vary along the profile and the observed correlation passes through the starting composition of fresh peridotite, which is also the terrestrial mantle composition (Fig. 5). In order to avoid confusion, we selected the data for potential iron ores, that is rocks with less than 20% silica and more than 50% Fe. The results taken from the literature are presented in Figs. 5 and 6. In Fig. 5, the correlation lies below the field of iron meteorites and it appears that for low Ni contents there might be some ambiguity between weathered meteoritic and lateritic compositions. Some of the scatter is due to the small size of analyzed samples (on the order of hundred mg) and we expect that the charge of a smelter (several kg) would exhibit less dispersion due to the averaging effect. The same is observed in Fig. 6. Some overlap is observed in the field representing the Umm el Marra iron pendant, which was shown to be the most weathered artifact.

More interestingly, the data for Kaman Kalehöyük, stratum II a (Figs. 4–6), overlap with the lateritic field but extend to

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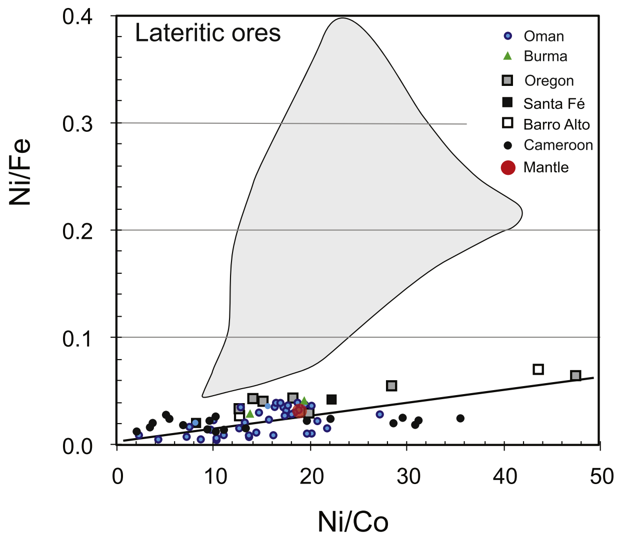

Fig. 5. Same as Fig. 1 for diverse lateritic iron ores. The trend for terrestrial iron is clearly different from that of extraterrestrial material. Barro Alto and Santa Fé (Brazil) are from Trescases and Oliveira, (1981), Cameroon from Yongue-Fouateu et al. (2006), Burma from Schellmann, (1989), Oregon from Hotz, (1967) and Oman from Al Kirbash, (2016). Terrestrial mantle composition falls on the same trend.

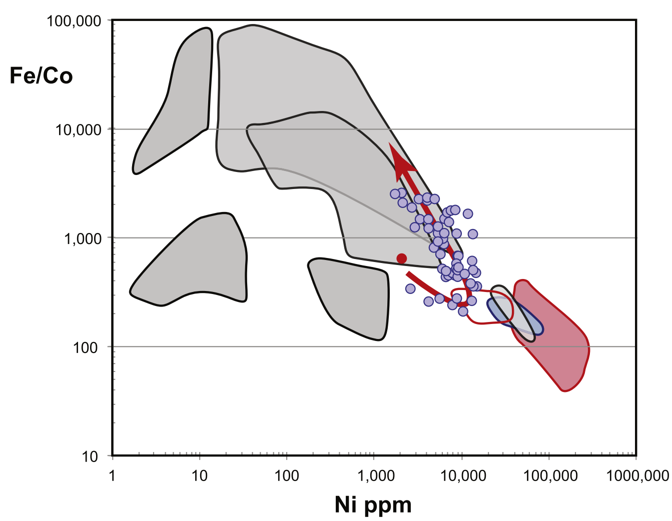

Fig. 6. Same as Fig. 4 for lateritic samples (dots; same set of data points as in Fig. 5). Notice the weathering path (red arrow) from the mantle value (red dot) with Ni increasing and then decreasing; the opposite being observed for Fe/Co. The fields for iron meteorites and iron artifacts from Fig. 4 are shown for comparison. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

significantly lower Ni contents. It is well known that such lateritic ores are commonplace in Anatolia (see e.g. Pigott, 1989).

These data however are for lateritic ores not metal. There is an additional possibility, which we did not consider yet: some fractionation might occur during the reduction process, thus changing the Ni/Fe and/or Ni/Co ratios. One obvious question then is whether some fractionation occurs between lateritic ores and the metal (Photos, 1987). This point will be discussed below.

2.5.2. Pyrrhotite

Some pyrrhotites (FeS) may contain significant concentrations of Ni. This is illustrated by the composition of pyrrhotite of the Oshirabetsu Mine, Hokkaido (Bamba, 1985; *On line supplementary material;* Table A3) ranging from 0.02 to 1.1% Ni. Their Ni/Fe (<0.02) and Ni/Co (0.5–39) plot along a trend below the terrestrial mantle correlation defined by laterites. They are significantly different from all meteoritic values and cannot explain the composition of Bronze Age irons.

3. Discussion

The starting point of this study was the controversy about the ultimate source of iron: meteoritic or smelted. According to previous results, the abundance of Ni in metal or the Ni/Fe ratio was considered a strong indicator of the origin of iron. We confirm that when the Ni is low, especially for weathered specimens, it is not sufficient as a criterion, whence the search for a more robust tracer of origin. According to the above results, the Fe/Co/Ni composition can provide the required information, which can be obtained using *p*-XRF. Analyzing several spots is highly recommended: on one single artifact, variable Ni is measured due to the extent of weathering, but the trend in a Ni/Fe vs Ni/Co appears to be a robust information as it permits to distinguish terrestrial from meteoritic iron.

3.1. The effect of weathering

The above results show that weathering of meteoritic iron affects the Ni content and the Ni/Fe ratio (Figs. 2–3). However, the Ni/Co and Ni/Fe variations still correlate. The low Ni/Fe ratio (or the Ni abundance) of terrestrial irons could be similar to that of some weathered meteoritic irons but at the same time their Ni/Co ratio does not fall on the correlation exhibited by meteoritic irons. The effect of weathering was ignored in most previous investigations but is now well established.

3.2. The effect of smelting

Photos (1989) found metal prills with comparatively high Ni/Fe ratios in some iron slags from Petres (N. Greece). It is noteworthy that no iron artifacts with high Ni content were ever found in the same context. The slags in question were high in iron oxide (wüstite) and contained small amounts of metal prills. She concluded that this could explain the abundance of Ni in all irons from the Bronze Age without the need of the extraterrestrial iron hypothesis. I cannot share this view and claim that the high Ni content of iron prills in slag ensues anytime, when the ore reduction fails. Ni is more easily reduced than iron, therefore if the smelting conditions were slightly too oxidizing, it is quite possible that nearly all Ni was reduced while only a small fraction of iron was. It can be shown that the fraction of Ni in the metal is a measure of the oxygen partial pressure in the furnace. The observed heterogeneity of Ni in the iron is a good indicator of out-of-control oxidizing conditions. Then a very small quantity of metal is obtained with a high Ni content (tens of %) if the starting ore contained some Ni. This is what the experiments of Photos (1989) yielded and possibly the case in Petres discarded slag as well. Extracting metal prills from a large quantity of slag would be a very hard task for little reward and most probably therefore the slag was discarded. The recovery of metal by a second smelting operation seemed questionable from an economical point of view. For this second reduction stage to be efficient, crushing the slag to permit exchange with carbon in the furnace would be required. This operation would have been too demanding when compared with using fresh ore. The experiments of Photos confirm our view. Some of the metal prills she analyzed after her smelting experiments contain up to 67% nickel. When starting from an ore with 1% NiO (0.7% Ni) and 72%

Fe_2O_3 (50% Fe), this suggests that only 0.3% Fe was reduced (for a metal with 20% Ni, 2.8% of Fe), a very poor yield! In addition the composition of chrome-spinel in the slag, indicates that 17% of its Fe is actually Fe^{3+} indicating that oxygen fugacity was close to the magnetite-wüstite buffer, that is far above the reducing conditions necessary to obtain iron metal.

Another important question is: are such Ni rich ores really common? I would say, in principle not. As already mentioned above, the best iron ores of the lateritic type contain little nickel (see also the discussion by Pryce and Natapintu (2009) on the quality of laterite in order to be a qualified iron ore). Those high in nickel (actually nickel ores as reported in Figs. 5–6) contain also quite large amounts of silica, which makes them poor iron ores; their color is orange yellowish and they look quite different from the true iron ores having a dark rusty color. This is because during the final stages of lateritization, silica and nickel (Ni^{2+}) are leached away, whereas Fe^{3+} remains immobile as iron oxides. It is important to notice that no smelted iron object of the Iron Age has been reported with significant amounts of Ni. In particular, the irons of Kaman Kalehöyük fall in the range 0.7 to 0.01% Ni (Akanuma, 2006), whereas numerous lateritic ores are present in Anatolia. According to their composition (Figs. 4–6) we think that Kaman Kalehöyük artifacts are good candidates for iron derived from lateritic iron ores. Such irons have Fe/Co higher than meteoritic irons and also higher than the lowest Fe/Co ratio of nickel rich ores, but the overlap is significant.

4. Conclusions

We conclude that it appears now important to measure correctly Bronze Age irons for their Fe:Co:Ni abundances, in order to determine whether or not, any specimen from that time is made from terrestrial iron. Replicate analyses are necessary since weathering leads to variably depleted Ni contents and a Ni content below 1% alone is no proof of origin; for Ni in excess of 1% the Ni:Co:Fe correlation will be conclusive. Scraps of rust are strongly biased samples, depleted in Ni and should be avoided, whereas oxidized artifacts are acceptable.

The present results complementing high quality analyzes from the literature suggest that (most or) all irons from the Bronze Age are derived from meteoritic iron, until some transition period, which occurred supposedly close to about 1200 BC. The next step will be to determine where and when terrestrial iron smelting appeared for the first time.

Acknowledgements

The author is indebted to P. Rochette for providing the Fe: Ni reference alloys. M. Fialin helped with EMP analyses. B. Zanda kindly provided the MNHN specimens. This work would not have been possible without the enthusiastic support of a number of archaeologist colleagues and curators. Musée du Louvre, in Paris (F. Bridey), Musée du Laténium in Neuchatel (D. Ramseyer), Musée National d'archéologie in St Germain en Laye (L. Olivier), National archaeology Museum in Aleppo (G. Schwartz, V. Matoian, A. Bilal and B. Jamouss); Petrie Museum, (S. Pancaldo) and UCL (Th. Rehren). M. Martinon-Torres (UCL) provided a bloomery iron sample from Gresham shipwreck. K. Mazurek permitted the analyses of the polished sections of Polish artifacts. A. Hmani provided a bloomery iron from Morocco. M. Hmani allowed the p-XRF measurements of a collection of iron meteorites. A. Muszynski (Poznan University) gave access to a collection of Morasko irons and provided a reference sample. R. Hewins patiently corrected my English. This research did not receive any specific grant from funding agencies in the public, commercial, or not-for-profit sectors.

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jas.2017.09.008.

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