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

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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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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.

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.

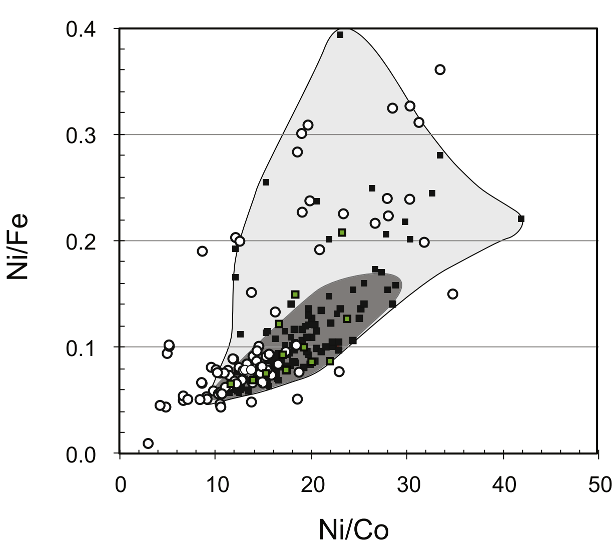

Fig. 1. Ni/Fe vs Ni/Co in iron meteorites. Black squares and gray area are from literature data for fresh iron meteorites (http://www.lpi.usra.edu/meteor/). Green squares: average compositions of the major iron meteorite groups (Mittlefehldt et al., 1998). White circles: *p*-XRF analyses of both polished 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.)

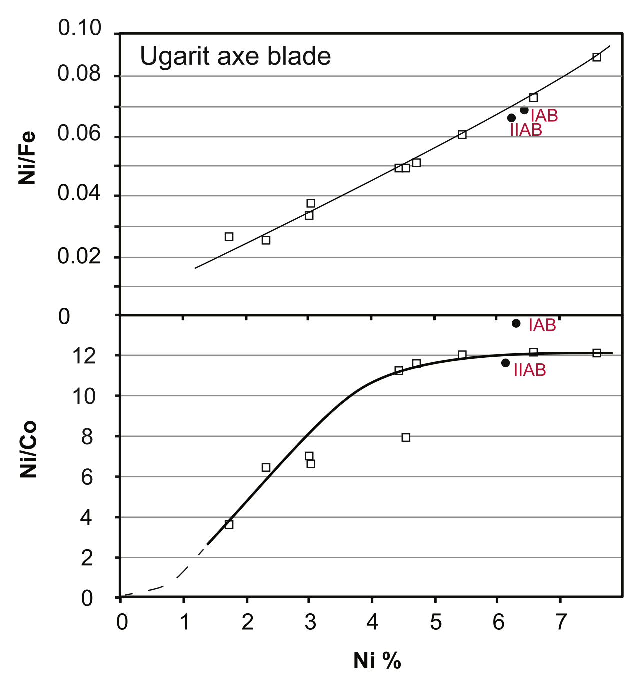

Fig. 2. Plot of Ni/Fe and Ni/Co against Ni abundance for Ugarit Axe. The steady variation of the Ni/Fe ratio against Ni indicates that Ni is preferentially leached during weathering whereas, Fe oxidized to Fe^{3+} is not. The Ni/Co ratio remains constant for mild weathering and then decreases when part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

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