

THE MAJOR AND TRACE-ELEMENT COMPOSITION OF THE WINONAITES: EVIDENCE FOR HETEROGENEITY AND IMPLICATIONS FOR GEOCHEMICAL ANALYSIS. Alison Hunt¹, Gretchen Benedix^{1,2}, Stanislav Strekopytov³, Catherine Unsworth³, Samantha Hammond⁴ and Phil A. Bland^{1,2,5}. ¹Impacts and Astromaterials Research Centre (IARC), The Natural History Museum, Department of Mineralogy, Cromwell Road, London, SW7 5BD, UK. ²IARC, Imperial College London, Department of Earth Science and Engineering, South Kensington Campus, London SW7 2AZ, UK. ³The Natural History Museum, Department of Mineralogy, Cromwell Road, London, SW7 5BD, UK. ⁴The Open University, Department of Earth and Environmental Science, Walton Hall, Milton Keynes, MK7 6AA, UK. ⁵Curtin University of Technology, Dept. Applied Geol., GPO Box U1987, Perth WA 6845, Australia. Email: alison.hunt@nhm.ac.uk

Introduction: Winonaites are primitive achondrites with roughly chondritic mineralogy and major element chemistry [1]. Additionally, some specimens contain relict chondrules [2]. These rare meteorites (as of 2010 there are 20 samples) are related to silicate inclusions in IAB iron meteorites via their oxygen isotope compositions [3].

Winonaites have abundant Fe-Ni metal and troilite (up to 12.5 and 19.9 vol%, respectively [1]). These components are often present as veins cross-cutting silicate portions, and are indicative of migration of a partial melt generated at the Fe, Ni-FeS cotectic (~950–980 °C [1, 4]). Additionally, they have textures which imply varying degrees of planetary processing, and brecciation. In particular, winonaites are characterised by heterogeneous grain-size and modal mineralogy, with some (Winona and Mt Morris) containing coarse-grained olivine-rich areas which may represent the residues of large degrees of melting, and others (Pontlyfni) containing fine grained areas enriched in plagioclase and high-Ca pyroxene which have been suggested to represent areas of crystallised basaltic melt [1]. Variable whole-rock rare earth element (REE) abundances and patterns also suggest that some partial melting and fractionation has occurred [5, 6]. Conversely, the winonaites and IAB silicate inclusions have been interpreted as the residues of low degrees of partial melting based on their chondritic FeO-MgO-MnO systematics [7], and previous major and trace-element data suggest that the winonaites are in fact surprisingly similar to CI chondrites [5, 7]. These discrepancies have previously been associated with heterogeneity in the winonaite samples and inconsistent sampling of REE-rich phosphates [5].

Hypotheses for the origin of the winonaite-IAB parent body include: 1) localized impact melt pools [8]; 2) incomplete differentiation [9]; and 3) incomplete differentiation followed by catastrophic impact break-up and reassembly [10]. New Ar-Ar and Hf-W ages for the winonaite-IAB body lend support to model 3), indicating incomplete core formation and differentiation, followed by impact [11, 12]. In this project we aim to produce a comprehensive geochemical dataset to better interpret the evolution of the winonaite-IAB parent body. Although less than 100 mg of powdered

sample is required to make a full analysis of major and trace-element chemistry, our initial goal is to assess the degree of bias introduced by analysing such small quantities of samples which are known to be heterogeneous on the thin-section scale.

Samples and Analytical Methods: We have samples of 5 winonaites (Winona, Fortuna, QUE 94535, NWA 1463 and Hammadah al Hamra 193) and 2 H ordinary chondrites (Ogi and Butsura).

Samples are powdered and dissolved for analysis by Inductively Coupled Plasma – Atomic Emission Spectroscopy (ICP-AES) to determine major and some minor elements, and Inductively Coupled Plasma – Mass Spectrometry (ICP-MS) for minor and trace elements. In an initial study of the winonaites, the dissolution technique resulted in an insoluble residue, which was determined to be chromite-rich. In order to determine the best method of dissolution for the winonaites, we are developing the digestion technique using H chondrites. These chondrites were selected because of their similar mix of metal/sulfide and silicate as well as the presence of chromite, which makes them a suitable (and abundant) material.

Major elements analysed at the Natural History Museum, London, by ICP-AES for this study include Mg, Al, Si, Ca, Ti, Mn and Fe. Major elements were determined by fusing 40 or 100 mg of sample with lithium metaborate flux in a ratio of 1:3, and dissolving the resultant glass bead in dilute nitric acid before analysis with a Varian Vista Pro ICP-AES. Minor and trace elements analysed include, among others, Sc, Ni, Sr, Zr, Ba, Pb, Th, U and the REE. Trace element concentrations were determined at the Natural History Museum and The Open University, by both ICP-AES (Varian Vista Pro) and ICP-MS (Varian 800 and Agilent 7500s) from HF-HClO₄ or HF-HNO₃ digestions of 50 mg powdered sample. The precision of analyses made by ICP-MS is routinely better than ±2.5 % (2 s.d.) for elements heavier than Ga, and 2 – 3.5 % for elements lighter than Ga.

Results: New major element data for Ogi and Butsura were determined using both 40 and 100 mg of powder. These samples have SiO₂ in the range 33.09 – 39.34 wt%. MgO ranges from 24.2 – 28.9 wt%, and Al₂O₃ between 1.84 and 2.19 wt%. The variation in

Fe_2O_3 is more restricted, between 38.0 – 39.2 wt%. These data compare well with literature values [13].

Analysis of a 50 mg split of Winona by ICP-MS provides the first concentrations of many siderophile trace elements in this meteorite, including Ga (14.7 ppm), Ir (0.30 ppm) and Pb (1.2 ppm). New data for Winona also include the first whole-rock determinations of many lithophile elements, including Sc (6.3 ppm), Sr (19.3 ppm) and Ba (30.9 ppm).

New analysis of Winona also reveals the highest concentration of light REEs analysed in a whole-rock sample of a winonaite, with values for La up to ~20 x CI (4.8 ppm; Fig. 1). These data show the most fractionated light REE/heavy REE pattern observed in winonaites, with heavy REE concentrations of < 2 x CI (Lu 0.04 ppm).

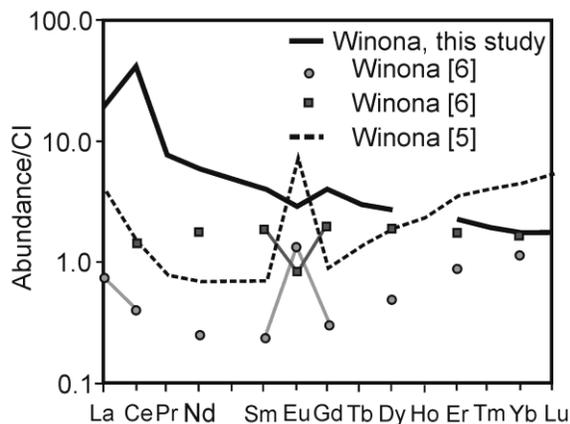


Figure 1. Winona REE abundance normalized to CI [14]. The preliminary results of this study are compared to previous whole-rock data [6] and calculated whole-rock REEs (based on mineral mode and analyses [5]) for Winona.

Discussion: With the exception of the light REEs and some siderophile elements (Ga, Ge and As), new data for Winona indicate that this sample has a low abundance of many elements when compared to the other winonaites [e.g. 15, 16]. However, no previous data exist for comparison for most siderophile and lithophile elements in Winona. The only data we can currently compare to previous analyses from Winona are the REEs.

Preliminary data for Winona suggest that some chips of this sample are more light REE-enriched than previously recognized. Such enrichment could potentially result from the variable modal mineralogy of these samples. In particular, over- or under-sampling of phosphates such as apatite will have a large effect on the abundances of the light REEs, due to their high concentrations in this phase. Using the concentration of light REEs recorded in apatites from Winona [5], a

simple mass-balance calculation reveals that the chip analysed for this study may have consisted of as much as 10 % apatite. However, this does not provide an adequate explanation for the heavy REE abundances of this sample, which are <2 x CI, as apatites from Winona are enriched in the heavy REE relative to light REEs and have abundances of these elements between 60 and 100 x CI. However, apatites from other winonaites do show light REE enrichment, similar to patterns seen in phosphates from the acapulcoites [5]. Therefore, the light REEs may be hosted in an alternative phase, or apatites from Winona may be more variably enriched in the REEs than previously recognised. Further work is needed to investigate the source of this high light REE signature.

Summary: Preliminary analysis of Winona indicates that this sample has low concentrations of most trace elements when compared to other winonaites. The light REEs are an exception to this, and portions of this meteorite appear to be significantly more light REE-enriched than previously thought. This variability may be a result of over-sampling phosphates such as apatite, and if this is the case it suggests that the winonaites are extremely heterogeneous. Further work will be undertaken on both Winona and other winonaites to verify this conclusion. As a result of this suspected heterogeneity, caution must be exercised when selecting chips of sample to be powdered. In particular, although full geochemical analyses can be conducted on <100 mg of powder, crushing larger chips should help to average out any heterogeneities.

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