EARLY OXIDATION AND LATE REDUCTION IN HIGH-Ni IRONS. C. M. Corrigan[1] and T. J. McCoy[1]. [1]Department of Mineral Sciences, Smithsonian Institution, National Museum of Natural History, 10th St. and Constitution Ave. NW, Washington, DC, 20560-0119. USA. Email: corriganc@si.edu.

Introduction: In this study, we continue our examination of the relationships between and formation mechanisms of iron meteorites, particularly high-Ni iron compositions. Corrigan et al. [1,2] and McCoy et al. [3] reported on the formation of and relationships between IVB irons and the Milton pallasite-South Byron trio irons (collectively MSB), respectively. Although these meteorites differ significantly, particularly in volatile siderophile abundances (Fig. 2), they share a number of common properties.

Similarities between IVB and MSB: The most intriguing results from oxygen isotope analyses of chromites in the IVBs and MSB [2,3] showed that, unexpectedly, the $\Delta^{17}O$ of the MSB meteorites ($\Delta^{17}O$ ~ -3.6 ± 0.6‰ (2SD)) was within error of measured values of $\Delta^{17}O$ of -3.4 ‰ (2SD = ±0.2) for Hoba and -3.4 ‰ (2SD = ±0.4) for Warburton Range, both IVBs (Fig. 1).

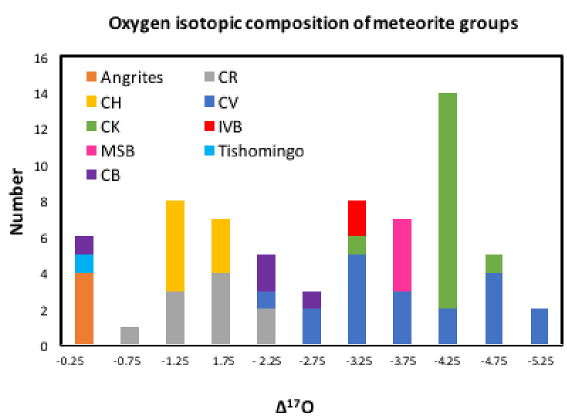

Figure 1. $\Delta^{17}O$ values in 0.5‰ bins with the central value shown of various meteoritic groups showing their relationship to IVB irons (red) and the Milton-South Byron trio (MSB, pink) [2]. Y-axis is the number of meteorites per bin.

IVB irons and MSB also exhibit isotopic similarities that may be indicative of formation location and/or timing. IVB irons were grouped with carbonaceous chondrites [4], as are most of the Ni-rich irons (IIC, IID, IIF). These irons are suggested to have formed 2-3 Myr after CAIs [4]. Recent work [5] suggests MSB also belong with the carbonaceous chondrite group.

Evidence for early oxidation: Most notable among the similarities is the high-Ni concentration, with IVB irons ranging from ~15.5-18 wt.% Ni [6] and MSB from ~15-18 wt.% Ni [7]. The high-Ni concentration of IVB irons was likely established during oxidation [8], as suggested by the fractionation of Fe relative to Co, Ni and Pd (Fig. 2), despite these elements having similar volatilities. [3] suggested the same for MSB. Oxidation of ~72% of the Fe in both IVB and MSB is required [3,8]. These authors suggested oxidation prior to core formation either in the nebula or during metamorphism via reaction with an oxidizing agent (e.g., ice).

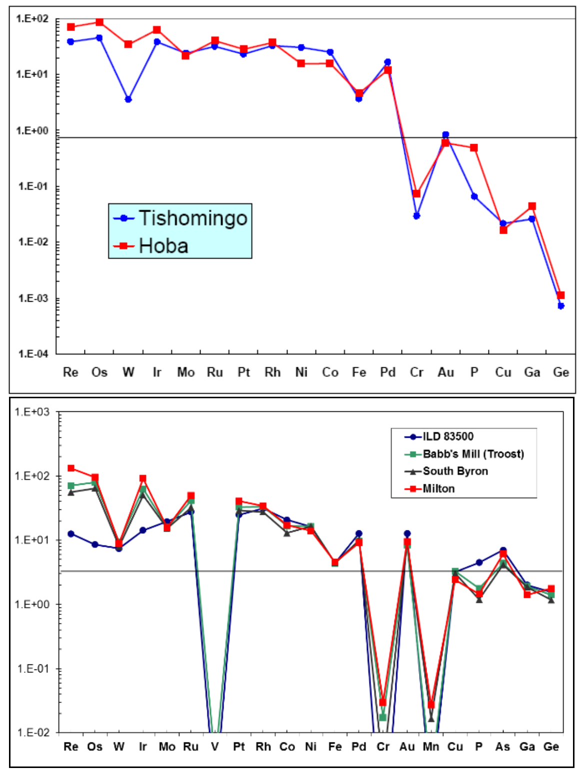

Figure 2. CI-normalized concentration of siderophle elements in the IVB iron Hoba, ungrouped high-Ni Tishomingo, and MSB [1,3]. Elements ordered by volatility.

Evidence for late reduction: While both IVB and MSB experienced oxidation, they also bear evidence for reduction in the mineralogy of the included phases. As first discussed by [9], several members of the IVB group contain both chromite ($FeCr_2O_4$) and daubréelite ($FeCr_2S_4$) (Fig. 3), suggesting that Cr occurs in both the oxidized and reduced form. Many members of IVB and MSB contain troilite, daubréelite, chromite, and schreibersite [10]. In IVB irons, daubréelite often occurs as lamellae within troilite (Fig. 3), while daubréelite in MSB occurs as grains of 2-5 µm within shock-melted and dispersed sulfides in South Byron and Babb's Mill (Troost's Iron) [3]. During the formation of these phases, [9] suggested that the IVB parent body was more oxidized than enstatite chondrites (EC), as IVBs lack Si in the metallic phase, though more reduced than "any other body". In addition to daubréelite, both IVB and MSB commonly contain schreibersite ($(Fe,Ni)_3P$), the reduced form of phosphorus. Daubréelite and schreibersite are more commonly associated with low-Ni (<7.5 wt.%) irons, including IIAB irons and low-Ni members of groups IAB and IIIAB. In contrast, high-Ni (>10 wt.%) members of these latter groups more commonly contain phosphates along with phosphides and lack daubréelite [10]. It is worth noting that the ungrouped, Ni-rich (32.5 wt.%) iron Tishomingo (Fig. 1) also appears to have experienced extensive oxidation [1], but contains daubréelite, similar to IVB and MSB.

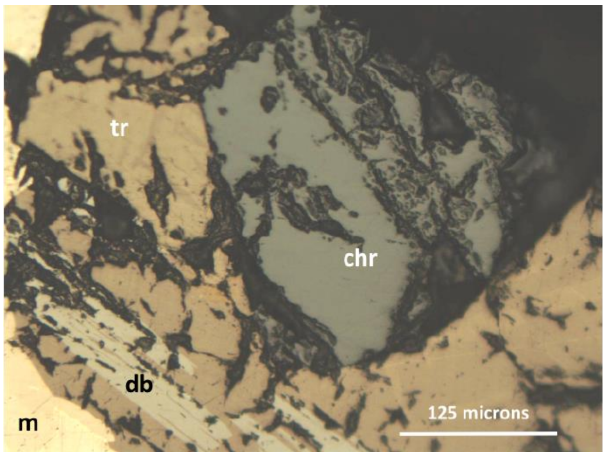

Figure 3. Chromite (chr) grain in Warburton Range in a matrix of troilite (tr), daubréelite (db) and metal (m) [2].

The suggestion that IVB was more reduced than all but ECs [9] was consistent with the suggestion, widely held at the time, that the depletion of siderophiles with increasing volatility reflected accretion at high temperatures (1200-1400K) from a gas of solar composition [11]. In contrast, [8,12] argued that no single temperature of condensation explains the IVB volatility trend. Instead, the high-Ni composition of IVB must result from oxidation [8] and the apparent inconsistency between oxidation to explain the metal composition and reduction to explain the presence of daubréelite reflects differences in timing.

While the high-Ni composition of the IVB parental melt was established during or before core formation, the coexistence of both chromite and daubréelite likely record conditions during low temperature, subsolidus exsolution [8]. These authors did not explore the mechanism by which the system evolved from oxidizing to reducing.

The co-existence of chromite and daubréelite suggests reduction near Cr-Cr_2O_3 buffer, at ~IW-5. In contrast, metal-silicate equilibrium is suggested to occur at ~IW-1 [8]. We discuss several mechanisms that may have interplayed to change the oxidation conditions.

Although sulfidization could have played a role, the co-existence of Fe^0 and FeS suggests the system was buffered at an fS_2 of iron-troilite, as originally suggested by [9].

If the system were buffered, a change in pressure could produce more reducing conditions. The C-CO buffer is pressure dependent, with the 1 bar C-CO buffer approximately 4 log units more reduced than the 100 bar C-CO buffer [13]. One mechanism that might produce such a drastic change in pressure late in the history of a parent body is removal of the silicate shell by impact. IVB and Tishomingo suffered early impact that stripped the silicate shell while the bodies were still hot [14]. Thus, impact stripping could have produced the change in oxidation conditions, although an argument against this idea lies in the fact that these meteorites lack graphite, indicative of buffering at C-CO.

Finally, introduction of a reductant, or exhaustion of an oxidant, could produce more reducing conditions at lower temperature. A reductant capable of producing reduction to the Cr-Cr_2O_3 buffer might be P. It is worth noting that Cr-Cr_2O_3 lies just below the $P+CaSiO_3=Ca_3(PO_4)_2+SiO_2$ buffer in T-fO_2 [15]. However, phosphate has not been observed in IVB, MSB or Tishomingo, arguing against a phosphide-phosphate buffer. A more likely scenario is exhaustion of an oxidant. If oxidation occurred with the idealized reaction $Fe^0 + H_2O = FeO + H_2$, loss of ~72% of Fe would require ~3 wt.% H_2O. Thus, reaction between metallic iron and oxidizing water could have occurred at high temperature, with the oxidant completely consumed in the formation of high-Ni irons. A possible argument against this mechanism is the apparent late formation (2-3 Myr after CAI) of irons grouped with the carbonaceous chondrites [4]. Limited heat production from decreased ^{26}Al might have been insufficient for melting of ice, alteration, complete melting and core formation, suggesting that at least a portion of oxidation occurred in the solar nebula prior to parent body accretion.

References: [1] Corrigan et al. (2005) *LPSC* #2062. [2] Corrigan et al. (2017) *LPSC* #2556. [3] McCoy et al. (2017) *LPSC* #2241. [4] Kruijer et al. (2014) *EPSL* 403, 317. [5] Hilton et al. (2018) this volume. [6] Wasson et al. (1989) *GCA* 53, 735. [7] Jones et al. (2003) *LPSC* 34 #1683 [8] Campbell and Humayun (2005) *GCA* 69, 4, 733. [9] Teshima and Larimer (1983) *Meteoritics* 18, 406-407. [10] Buchwald (1975) *Iron Meteorites*. UC press. [11] Kelly and Larimer (1977) GCA 41, 93. [12] Rasmussen et al., (1984) *GCA* 48, [13] Benedix et al. (2005) *GCA* 69, 5123. [14] Yang et al. (2014) *GCA* 124, 34. [15] Robie et al. (1978) USGS Bull. 1452.