Investigation of Chondritic Metal Oxidation States by X-Ray Photoelectron Spectroscopy

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Introduction: Ferromagnesian silicate composition, sulfur distribution, and Cr_2O_3 within olivine are considered reliable indicators of petrological grade in ordinary chondrites. At the onset of thermal metamorphism, Cr_2O_3 in Type II chondrule olivine decreases from ~0.5 to <0.1 wt % [1–3]. As metamorphism progresses, S conglomerates with troilite and Fa content of chondrule olivine homogenizes [4]. Oxidation states of Cr^{3+} and Fe^{2+} are normally assumed, but the chemical environment is rarely investigated because typical methods of analysis such as SEM-EDX do not provide such data. X-Ray Photoelectron Spectroscopy (XPS) is a surface sensitive technique that collects chemical state information on a microanalytical scale. The proportional valence of chondritic metals is linked to their metamorphic histories, and may be evident of an oxidative or reductive relationship between Type I and Type II chondrules [5]. Used in complement with SEM-EDX, it is expected that XPS can assess oxidative trends in tandem with metamorphic trends as chondritic olivine should contain a mixture of Cr and Fe in different valence states [6,7]. NWA 4910, NWA 7029, NWA 11291, and NWA 11344 are ordinary L and LL chondrites representing a range of petrological grades between 3.1-4. They were surveyed with SEM-EDX for initial classification and select areas of interest were explored further with XPS analysis.

Method: Thick sections were coated with ~10 nm carbon via physical vapor deposition. Sites of interest were identified with a Zeiss Sigma VP FEG SEM at Portland State University's Center for Microscopy and Nanofabrication before an Oxford Scientific Energy-Dispersive X-Ray spectrometer was used to quantify elemental composition. When necessary, samples were stripped of Carbon before being analyzed with the Versa Probe II XPS. AZtec and MultiPak were used for processing data from SEM-EDX and XPS, respectively.

Petrological grade: Fa content in chondrules was surveyed for each meteorite and used to assess homogenization of olivine and identify Type I and Type II chondrules. In NWA 4910 and NWA 7029, Fa content varied widely, indicating unequilibrated meteorites. Forsteritic olivine in chondrules from NWA 7029 and 4910 each had a Cr content ~0.5 wt %, suggesting a metamorphic grade near 3.1 for both. Matrix S around chondrules in both chondrites was diffuse, as expected for an unequilibrated chondrite. In NWA 11291 chondrule olivine had largely equilibrated and S around chondrules was present in troilite. NWA 11344 was a brecciated mix of L3 and L4 components, likely due to shock, as evidenced by numerous shock veins filled with FeO and FeS. Matrix olivine had equilibrated, but chondrule olivine indicated a wide range of Fa contents. Further, S surrounding several chondrules was diffuse in the matrix, indicative of a low petrological grade of some chondrules.

X-Ray Photoelectron Spectroscopy: XPS was used to characterize chondrule and matrix olivine. Survey scans showed a relative enrichment of Cr and Ca, and a relative depletion of Fe and S in chondrules, in agreement with SEM and EDX data. High resolution scans of a Type II chondrule characterized O 1s and Fe $2P_{3/2}$, which were each deconvoluted into two peaks. O 1s had peaks at 530.8 eV (FWHM=1.74 eV) and 531.8 (FWHM=2.18 eV) while Fe $2P_{3/2}$ had peaks at 710.2 eV (FWHM=2.9) and 713.4 eV (FWHM=5.5 eV). The 530.8 eV peak is likely a Si-O-M moity in olivine, as observed by Zakaznova-Herzog et al. [8]. The 531.8 eV peak may be a Si-O-Fe peak of higher valence Fe. The 710.2 eV and 713.4 eV peaks fit Fe^{2+} and Fe^{3+} in approximately equal proportions, likely in olivine [7].

Troilite Enriched Mesostasis: One type IA chondrule in NWA 7029 had a mesostasis composed primarily of Fe and enriched in S, with troilite composing a large part of the mesostasis. Low petrological grade and low potential for shock mobilization suggest the S is primary [9]. While this chondrule can be fit into the existing classification schemes, it differs substantially from other Type I chondrules and may be fruitful for further exploration.

Conclusion: XPS used in complement with SEM-EDX can collect otherwise unavailbable information about the chemical state and environment of chondrules, such as the proportion of Fe^{2+} to Fe^{3+}. Further XPS investigations may be able to shed light on longstanding questions such as the relation of Type I and Type II chondrules, thought to be related by oxidative or reductive processes.

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