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IRON OXIDATION STATE OF AMORPHOUS SILICATES AND LOW-LOSS ELECTRON ENERGY SPECTROSCOPY OF ORGANIC MATTER IN THE PRISTINE CM CHONDRITE MARIBO.

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Introduction: Mighei-type (CM) carbonaceous chondrites have recorded complex parent-body processes such as brecciation and aqueous alteration. Investigations of the weakly altered members of this meteorite group are of particular importance to disentangle variable alteration modes on the CM parent body and to infer relationships to other meteorite classes such as the more primitive CR chondrites. The Maribo CM chondrite was collected shortly after its observed fall in Denmark in 2009 [1]. Its bulk oxygen isotopic composition ($\Delta^{17}\text{O} = -3.85\text{‰}$) plots towards the less altered end of the CM suite, close to the CM chondrite Paris ($\Delta^{17}\text{O} = -3.39\text{‰}$), regarded as one of the most primitive CM chondrites [e.g., 2]. Initial petrographic studies of Maribo have shown that it hosts unusual alteration features [3,4], and its chemical characteristics places it well above the maximum petrologic type 2.6 of other CMs [1]. Here we have initiated an electron microscopy study of the fine-grained matrix components and organic matter (OM) of Maribo to compare it to other pristine chondrites such as Paris [2], CRs [5] and Acfer 094 [6].

Methods: The C- and N-isotopic compositions of Maribo matrix were studied by NanoSIMS applying standard ion imaging protocols [7]. Specific mineral assemblages were prepared for transmission electron microscopy (TEM) by the focused ion beam (FIB) technique. Overview brightfield and high resolution imaging of matrix regions was performed with an aberration-corrected FEI/ThermoFisher Titan “Themis” (300 kV) at Münster University. Electron energy loss spectra (EELS) at the Fe-L edge were acquired with the Münster Zeiss Libra 200FE (200 kV) using the protocol by [6]. Low-loss and core-loss EELS of ¹⁵N-anomalous organic matter were acquired with a monochromated, aberration-corrected Nion UltraSTEM 100MC (60 kV) at the SuperSTEM Laboratory.

Results and Discussion: Amorphous Silicates. The majority of Maribo matrix regions within the FIB lamellae studied here consists of coarse-grained Fe-rich phyllosilicates (cronstedtite) intermingled with fine-grained areas of “spongy” nano-phyllosilicates. Within these Fe-poorer, fibrous regions, small (a few 100 nm) patches of amorphous silicate material (ASM) exist that do not show signs of crystallization in electron diffraction and high resolution mode. Abundant porosity as in Paris [5] or Acfer 094 [7] is not observed in the FIB sections studied here. Fe,Ni-sulfides occur throughout the fine-grained regions, but no nm-sized Fe,Ni metal grains could be found. Nevertheless, Maribo indeed contains large kamacite grains within its matrix regions [1]. $\text{Fe}^{3+}/\text{Fe}_{\text{total}}$ ratios of several ASM regions range from 0.68 to 0.83 (mean 0.72 ± 0.05). Interestingly, this is higher than measured by synchrotron analyses on bulk CM chondrites [8], but within the range observed for CR/Acfer 094 matrices [6,9]. This can be explained by the onset of aqueous alteration and initial hydration of susceptible ASM before mobilization of Fe^{3+} into larger phyllosilicates and magnetite [e.g., 6,9]. This indicates that the ASM regions of the Maribo matrix have recorded a similar degree of hydration as the matrices of the most primitive chondrites.

Organic Matter. A minor fraction of Maribo OM shows ¹⁵N-depleted isotopic compositions ($\delta^{15}\text{N}_{\text{air}} \sim -200\text{‰}$) occurring as submicron organic aggregates. In the TEM, this OM is dispersed as small particles within the matrix. C-K edge functional chemistry is dominated by the typical ~285 eV onset indicative of aromatic rings as well as ketone/carbonyl (~286.6 eV), aliphatic (~287 eV), and carboxyl (~288 eV) functional groups with varying intensity on the nm scale, which has been observed in CR and IDP organics as well [e.g., 10]. In contrast to OM in CRs, which often exhibits a globular, well-defined texture (probably due to fluid reactions), this morphological and chemical small-scale variability may attest to a more pristine nature of the Maribo OM, which is supported by analyses on extracted bulk material [1]. For the first time, low-loss spectroscopy of OM by monochromated STEM-EELS ($\Delta E \sim 0.02$ eV) showed the presence of D- and G-bands, well-known from Raman spectroscopy, at energy losses of ~0.16 eV and ~0.2 eV, respectively. Future analyses of these vibrational energy loss bands in the TEM may provide further insight into the functional makeup of complex OM on a scale not accessible by standard Raman spectroscopy.

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