THE EARLY STAGES OF AQUEOUS ALTERATION IN CM CHONDRITES – TEM-ULTRASTEM-STXM INVESTIGATIONS OF THE LESS-ALTERED CHONDRITE MARIBO. C. Vollmer[1], M. I. F. Barth[2], C. Le Guillou[3], Q. Ramasse[4], M. Horstmann[2], A. Bischoff[2]. [1]Universität Münster, Institut für Mineralogie, Germany, christian.vollmer@wwu.de; [2]Universität Münster, Institut für Planetologie, Germany; [3]Ruhr-Universität Bochum, Institut für Geologie, Mineralogie and Geophysik, Germany [4]SuperSTEM, Daresbury Laboratory, UK.

Introduction: CM carbonaceous chondrites are breccias which recorded complex alteration reactions in the early solar system [1,2]. Alteration occurred either on the final parent body [1], on primary accretionary embryos [2], in the nebula in temporarily ice-enriched regions [3] or in all of these settings. There is indication that some sulfides may form via condensation [4] and that certain large cronstedtites in CMs may have been altered prior to final accretion [5]. Recently, a ^{17,18}O-enriched magnetite-pentlandite "cosmic symplectite" (COS) has been found in Acfer 094 pointing towards a condensation origin [6]. Here we investigated tochilinite-cronstedtite intergrowths (TCI) and other alteration features in the recent CM fall Maribo [7] by in-situ techniques. The bulk oxygen isotopic composition of Maribo (Δ^{17}O = -3.85‰) plots towards the less altered end of the CM suite, close to the CM chondrite Paris (Δ^{17}O = -3.39‰) and the CCAM line [8]. Petrographic studies [7] have shown that Maribo hosts primitive mineral assemblages, and its chemical characteristics places it well above the maximum petrologic type 2.6 of other CMs. It is therefore a key sample to study early stages of aqueous alteration in CMs and to distinguish nebular and parent body processes.

Methods: A thin section of Maribo was studied by SEM, specific mineral assemblages were prepared for TEM analysis (Jeol 3010 and Zeiss Libra 200FE at the University of Münster) and Scanning transmission X-ray microscopy (STXM) by FIB. In-depth investigation of some of the nanocrystalline samples was performed on an aberration-corrected dedicated scanning TEM (Nion UltraSTEM 100) at low beam voltage (60 kV). STXM at the Fe-$L_{2,3}$ edge was performed on two FIB samples at the Canadian Light Source to determine the valence state of iron. The samples were investigated before TEM to avoid modification of Fe^{3+}/Fe_{total} ratios.

Results: Maribo contains larger cronstedtite and tochilinite grains than commonly found in CM chondrites, with sizes up to several hundred µm [7]. Large tochilinites are compact, typically surrounded by a very fine-grained rim and either isolated in the matrix or in the direct vicinity or within chondrules. A second distinct type of tochilinite in Maribo shows intergrowth with serpentine and forms a strongly layered texture initially called "fishbone-tochilinite" [7] (Fig. 1a). Oxygen and sulfur concentrations of these layered TCI are very similar compared to the more compact tochilinites. Two studied FIB sections from this material demonstrate that they are in fact layers of crystalline tochilinite stacks alternating with porous serpentine bands having very small crystalline domains. The sizes of the alternating bands are on the order of a few hundred nanometers. In another FIB section, the material consists of layers made of magnetite, pentlandite and pyrrhotite nanocrystals. It also contains some weakly crystalline Si-rich material and an interstitial carbonaceous groundmass (Fig. 1b). The contrast difference in the layers of this material is less pronounced, but mainly due to different densities of particles.

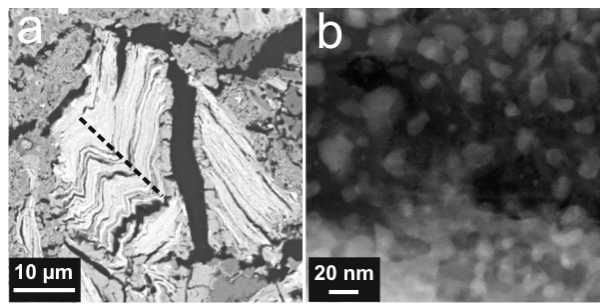

Figure 1. a – SEM-BSE image of a typical layered TCI in Maribo with the direction of the FIB section indicated; b – UltraSTEM-HAADF image of nano-oxides and –sulfides of different densities in an amorphous groundmass.

Another unusually zoned object (MAR21) previously described in [7] consists of a core of compact tochilinite, an intermediate layer of a fibrous Fe-oxide and an outer, texturally homogeneous rim with a composition between tochilinite and cronstedtite (Fig. 2a). The outer TCI-like rim displays diffuse electron diffraction patterns across the entire region, but HR imaging shows some short-range order indicative of protocrystalline material. It has a fibrous texture and a high porosity that gradually increases from the outside inwards (Fig. 2b).

Two FIB sections from Maribo were investigated by STXM. These have been prepared across the zoned object with the protocrystalline TCI-like rim described above (Fig. 2) and from the interface between an altered barred olivine chondrule and the matrix. Fe^{3+}/Fe_{total} ratios are heterogeneous across different areas but vary mostly between 0.5-0.6. The protocrystalline TCI-like rim shows a slightly increasing Fe^{3+}/Fe_{total} ratio from the outside towards the interior.

The heterogeneous Fe valence in the matrix of the other section seems to correlate with different Fe abundances as inferred from STEM-EDX maps. Where the Fe content is a bit lower, the Fe^{3+}/Fe_{total} seems to increase.

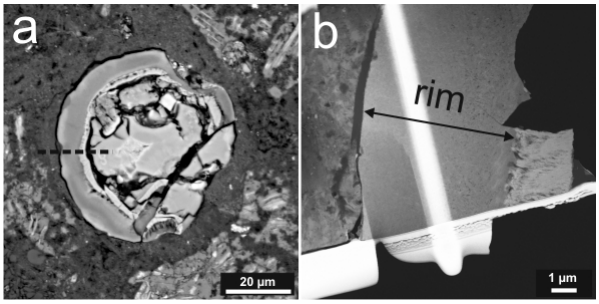

Figure 2. a – SEM-BSE image of zoned object MAR21 in Maribo with the direction of the FIB section indicated. See text for details; b – STEM-HAADF image of the protocrystalline rim. The bright bar is a thicker part of the section left over for stabilization.

Discussion: TCI grains are common in CM chondrites and have a complex structure of intercalated sulfide-hydroxide-silicate layers [e.g., 9]. The layered TCI grains observed in Maribo are rather uncommon, first because the size of the individual layers is larger than usually observed, but most importantly because the nanocrystalline texture in one FIB section is similar to the COS material from Acfer 094. Remarkably, comparable, but much smaller (~1 µm) layered Fe-O-S-Ni-rich grains have been recently reported in pristine CR chondrites MET00426 [10] and GRA95229 [11]. In GRA95229, TEM investigations have shown that contrast differences are also due to nanocrystals of Fe-oxides and sulfides. Because aqueous alteration in CRs is less advanced than in CMs, the layered nanocrystals showing bulk tochilinite composition may mark a first step in the evolution of tochilinite formation. Similar grains have not been reported in the CM chondrite Paris, which is assumed to represent one of the least altered CMs so far similar to Maribo [8]. It is therefore likely that this material only forms under very restricted alteration conditions, maybe before final accretion in the nebula [6]. Alternatively, the nanocrystalline texture might result from the breakdown of tochilinite into simpler oxides and sulfides by a heating event. However, the occurrence of very similar grains in primitive CR chondrites with abundant organics that have experienced virtually no thermal overprint seems to rule out this possibility. The layered texture was probably inherited from a kamacite precursor showing microstructures indicative of martensitic transformation due to rapid cooling or a sulfide precursor with exsolution features [6,9]. The survival of this texture would therefore underline the overall weak alteration overprint. The protocrystalline TCI in the rim of the object MAR21 is another hint for this weak alteration stage, as it can represent the first step of serpentine/tochilinite nucleation. On the other hand, evolution of unusually large TCI grains in Maribo points towards a more advanced stage of alteration. These grains, which also often have a fine-grained rim, could therefore support a preaccretionary scenario, e.g., alteration on a primary accretionary embryo before incorporation into the final parent body [2].

Redox conditions on the CM parent body have been investigated by in-situ techniques [12], and values may partly be compared to observations in terrestrial serpentines [13] and thermodynamic modelling. The results from Maribo imply that the redox state varies within microscale subareas of the matrix. The overall Fe^{3+} abundance in Maribo is lower than in CR chondrites [14]. [13] have shown that Fe valences in serpentines strongly depend on the water:rock ratio, so it is possible that observed heterogeneities are due to different fluid availabilities. Precursor chemistry and reaction kinetics play an important role as well.

Conclusions: We have investigated the nanoscale mineralogy of TCI grains and other alteration features in the CM chondrite Maribo by combining TEM and STXM techniques. We found the presence of a nanocrystalline sulfide-oxide material similar to the COS found in Acfer 094, strongly layered TCI grains and unusual textures like a protocrystalline TCI-like rim. These observations all support the suggestion by [7] that Maribo is one of the least altered CM chondrites so far in our collection.

We acknowledge support by the DFG (SPP 1385-2). The SuperSTEM Laboratory is supported by the U.K. Engineering and Physical Sciences Research Council.

References: [1] Brearley A. J. (2006) *MESS II*, 587-624. [2] Bischoff A. (1998), *Meteoritics & Planet. Sci.* 33, 1113-1122. [3] Ciesla F. J. et al. (2003) *Science 299*, 549-552. [4] Harries D. and Langenhorst F. (2013), *Meteoritics & Planet. Sci. 48(5)*, 879-903. [5] Howard K. T. et al. (2011) *GCA 75*, 2735-2751. [6] Seto Y. et al. (2008) *GCA 72*, 2723-2734. [7] Haack H. et al. (2012), *Meteoritics & Planet. Sci. 47*(1), 30-50. [8] Hewins R. H. et al. (2014), *GCA 124*, 190-222. [9] Tomeoka K. and Buseck P. R. (1985), *GCA 49*, 2149-2163. [10] Le Guillou C. and Brearley A. J. (2013), *GCA*, in press. [11] Leitner J. et al. (2012), *Meteoritics & Planet. Sci. 47*, A243. [12] Beck P. et al. (2012), *GCA 99*, 305-316. [13] Klein F. et al. (2009), *GCA 73*, 6868-6893. [14] Le Guillou C. et al. (2014), this volume.