EXPERIMENTAL MAGNETITE FORMATION UNDER PROTOSOLAR CONDITIONS.

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Introduction: Regions of the solar protoplanetary disk enriched with ices and heated by shockwaves have been suggested as environments of rapid gas-solid interactions [1], [2]. Metallic minerals (e.g., kamacite, taenite) are expected to be highly reactive under such conditions even at relatively low temperatures of 200 to 600 °C [3]. The formation of magnetite is expected via the reaction of Fe-rich metal with water, given that the H_2/H_2O ratio provides a sufficiently high oxygen fugacity. In order to better understand the reaction and growth mechanisms and the resulting morphology of the magnetite formed, we set up a gas-mixing furnace capable of operating in the pressure range of 1 to 100 mbar.

Experimental Methods: The low-pressure gas-mixing furnace consists of a horizontal quartz glass tube heated inside a tube furnace. The tube is evacuated via a chemically resistant scroll pump and the effective pumping speed is adjusted via a set of needle valves. On the inlet side gas mixtures are provided by three mass flow controllers for the gases H_2, N_2 and H_2S, and a controlled evaporator/mixer (CEM) for H_2O. Unlike a bubbler system the CEM approach allows vaporizing any liquid, residual-free solution into the low-pressure furnace without fractionation between the liquid and gaseous phases. The flow of liquid is precisely measured and regulated via a Coriolis flow meter in the range of 0.2 to 5 g/h. To date experiments have been conducted in H_2+H_2O mixtures at temperatures of 350, 450 and 600 °C, H_2/H_2O ratios of 1.00, 2.51 and 9.65, and pressures of 1 and 10 mbar. Run durations ranged between 3 to 25 hours. Starting material were 10x10x0.75 mm^3 pieces of Fe-Ni-Co-Cr alloy with approximately chondritic composition. Prior to the experiments the metal plates were polished and cleaned by Ar^+ ion sputtering. After the experiments the reacted surfaces were imaged by SEM and cross-sectioned by FIB.

Results: Among the parameters studied, temperature exerts the strongest influence on the morphology and growth mechanism of magnetite.

At 350 °C/10 mbar magnetite grows as coherent, columnar layers with relatively low porosities and poorly developed euhedral crystal faces at their surfaces. The thicknesses of the layers show bimodal distributions and depend on the local crystallographic orientation of the metal substrate. Preliminary evaluation shows that magnetite growth follows a parabolic rate law with an averaged rate constant of approximately 0.03 μm^2/h.

At 450 °C/10 mbar magnetite crystallizes as coarser-grained, mostly skeletal crystals. The layers are coherent and porosities vary greatly. Octahedral and twinned, platelet-shaped crystal occur. In cross section the magnetite layers frequently show protrusions into the metal substrate. Epitaxial growth can be observed, but the layer thicknesses are much more uniform compared to 350 °C.

At 600 °C/10 mbar the magnetite layer develops as a voluminous framework of relatively well-formed octahedral crystals. Magnetite whiskers with lengths up to several µm and diameters of several 10s of nm occur. Epitaxial growth is common but protrusions into the metal substrate occur only rarely. Reducing the pressure to 1 mbar results in the development of a continuous layer of magnetite with greatly reduced growth of individual octahedrons and whiskers. The linear growth rate at 10 mbar is approximately a factor 3.4 higher than at 1 mbar.

Discussion: The largely different morphology of the magnetite layer grown at 600 °C indicates a fundamental change in the growth mechanism between 450 and 600 °C. So far magnetite whiskers are not known from chondritic meteorites such as Acfer 094 [4], suggesting that if metal-gas reactions took place, T and P were either low or other gas components such as H_2S inhibited the growth of whiskers. Compared to previous experiments by [3], the rate constant determined at 350 °C appears to be substantially larger by at least two orders of magnitude. Preliminary observations from the experiments suggest that sample cleanliness (in particular in terms of trace hydrocarbons) and the flow regime (laminar vs. turbulent flow) play important roles in determining the rate of reactions, both in the laboratory and solar nebula.

References: [1] Ciesla F. J. et al. 2003. *Science* 299:549–552. [2] Harries D. et al. 2015. *Nature Geoscience* 8:97-101. [3] Hong Y. and Fegley B. 1998. *Meteoritics & Planetary Science* 33:1101-1112. [4] Barth M. I. F. et al. 2015. *Meteoritics & Planetary Science* 50:A43.

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