Site-selective Cation Transport in the Near-Surface Region of Magnetite (001)

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The structure and composition of its near-surface region strongly influence the performance of magnetite (Fe_3O_4) based catalysts and devices. Phenomena like oxidative regrowth and the formation and lifting of the subsurface cation vacancy reconstruction suggest a cation transport process altering the structure of magnetite's near-surface region [1-3]. Cation transport induced by step-wise vacuum annealing was monitored at the interface of a homoepitaxially grown $^{57}Fe_3O_4$ thin-film and its natural Fe_3O_4 (001) single crystalline substrate. The ^{57}Fe distribution, stoichiometry and electron density of the thin-film were monitored simultaneously by nuclear forward scattering and X-ray reflectivity at the P01 beamline at PETRAIII [4]. Joint fits of time spectra (TS) and nuclear resonant reflectivity (NRR) measured after each annealing step provided site-selective ^{57}Fe distribution profiles indicating cation transport occurring predominantly via the octahedral sublattice as expected under oxidizing conditions starting from 470 K on [5]. Diffusion coefficients on the order of 10^{-22} m^2/s, much lower than predicted by bulk diffusion models [6], suggest that near-surface cation diffusion might be influenced by surface reactions counteracting the diffusion of ^{57}Fe into the substrate.

The diffusion experiments are complemented by a structural characterization of the magnetite thin-film by surface X-ray diffraction measured at the SixS beamline at SOLEIL further emphasizing the link between structure, stoichiometry and transport processes in magnetite.

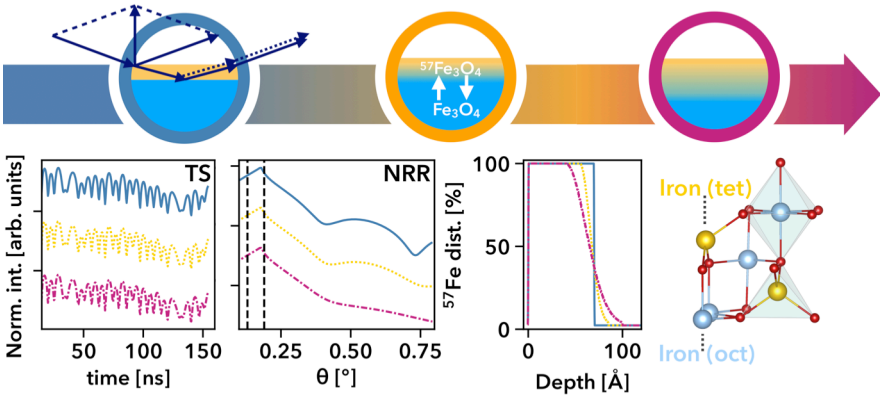

Fig. 1: Scheme of the cation transport experiment. Cation interdiffusion in a $^{57}Fe_3O_4/Fe_3O_4$ sample upon annealing was monitored by nuclear forward scattering in specular geometry. Site-selectivity for octahedrally and tetrahedrally coordinated ^{57}Fe cations was achieved by measuring TS while NRR provided depth selective information about the ^{57}Fe distribution. Simulated TS and NRR corresponding to the degree of cation intermixing in the scheme above are shown.

References: [1] S. Nie *et al. JACS* **135**, 10091 (2013); [2] R. Bliem *et al. Science* **346**, 1215 (2014); [3] B. Arndt *et al. Surf. Sci.* **653**, 76 (2016); [4] M. Andreeva *et al.*, *Mosc. Univ. Phys. Bull.* **63**, 132 (2008); [5] K. Becker *et al.*, Phys. Chem. Solids **54**, 923 (1993), [6] R. Dieckmann, *Ber. Bunsenges. Phys. Chem.* **81**, 344 (1977)