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Interaction of Fe and Fe_2O_3 with reactive gases

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Introduction

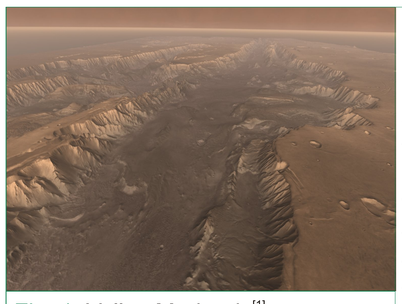


Fig. 1: Valles Marineris[1]

Mars' atmosphere contains methane and formaldehyde with 10 ppb respectively 100 ppb. Different sources including extraterrestial life have been proposed, but the origin of these gases is still unknown. It has been found earlier that methane and formaldehyde can be produced through a photocatalytical process on a hematite surface with adsorbed water in a CO_2 atmosphere.
The scope of this work is to examine the underlying processes which happen on granular powders of hematite. As a first step thin films of iron and Fe_2O_3 are examined.
These thin films are investigated by means of their interaction with O_2. These reactions have been studied with photoelectron spectroscopy. X-ray photoelectron spectroscopy is used to determine stoichiometry of the samples, while Ultraviolet photoelectron spectroscopy and Metastable Induced Electron Spectrocopy are used to analyse the valence band region and to gain information about changes in workfunction due to reactions on the surfaces.

As a next step the photocatalytical process found in [2] is investigated in detail. The work shown here is necessery to built up an own data set for forthcoming measurements and correct interpretation of further work.

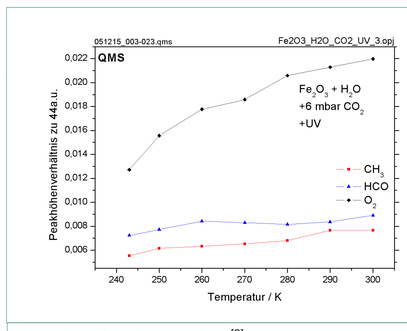


Fig. 2: CH_4 formation[2]

Experimental technique: MIES

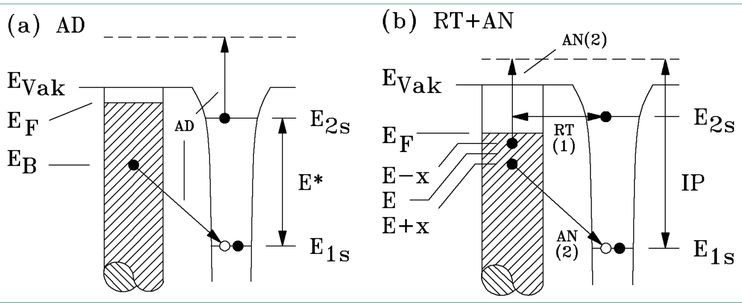


Fig. 3[3]: (a) MIES AD
(b) MIES RT+AN

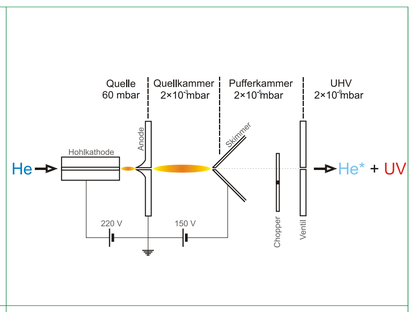
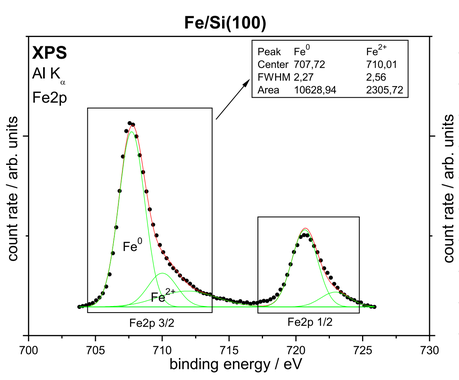
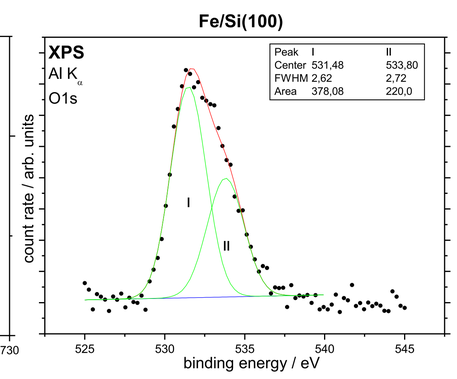


Fig. 4[3]: MIES setup

Thin Iron Films

For preparation of clean iron films, an electron beam evaporator (EFM 3 by Omicron) filled with a rod of pure Fe (99,95 %, 2 mm diameter; Goodfellow) has been used. Typical flux varied between 150 nA and 300 nA, evaporation duration between 5 min and 45 min and film thicknesses between 2.6 nm and 16 nm.

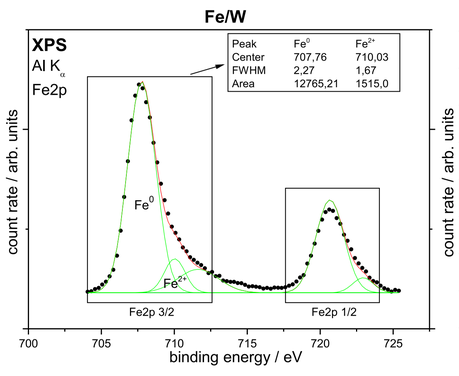


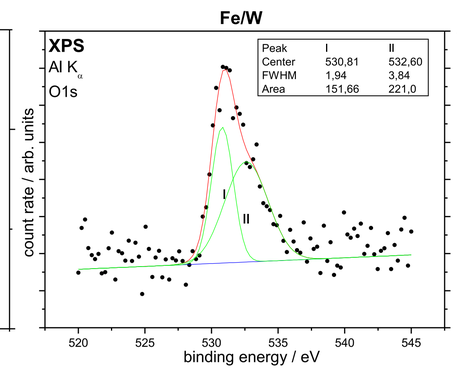


Si substrate:

- Fe^0 FWHM: 2.27 eV
- surface contaminated with oxygen
- 15 % of the surface consists of FeO
- O 1s consists of two species, peak II is assigned to unco-ordinated oxygen

⇨ substrate change due to formation of $FeSi_2$





W substrate:

- sputtered sample shown, film thickness 16 nm
- only 10 % of the surface consists of FeO
- same Fe^0 FWHM

References

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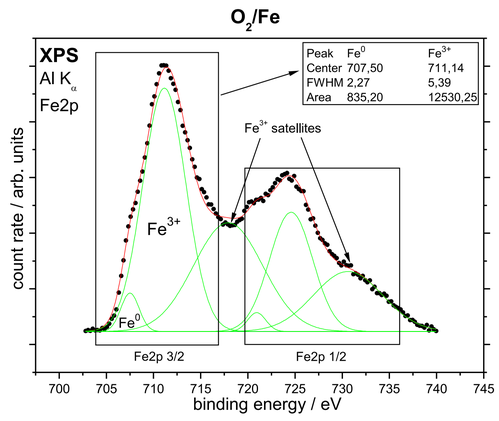
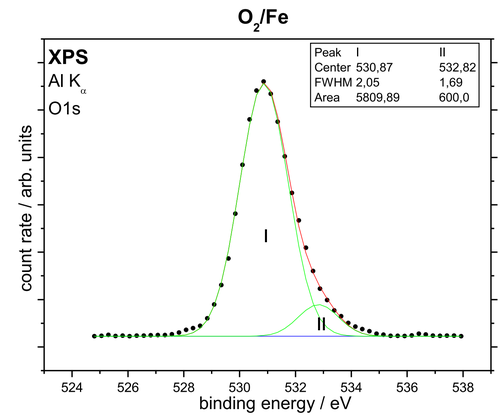
O_2 on iron films

The preparation of the Fe_2O_3 film on W has been carried out as described in [4] and [5]. In short, a first thin iron film is oxidized, then iron evaporated again,followed by oxygen offer. This cycle is repeated several times. During this procedure the substrate is heated at a temperature of about 450 °C.



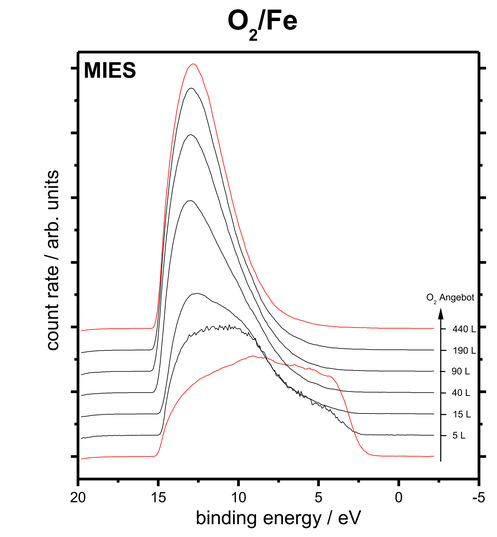


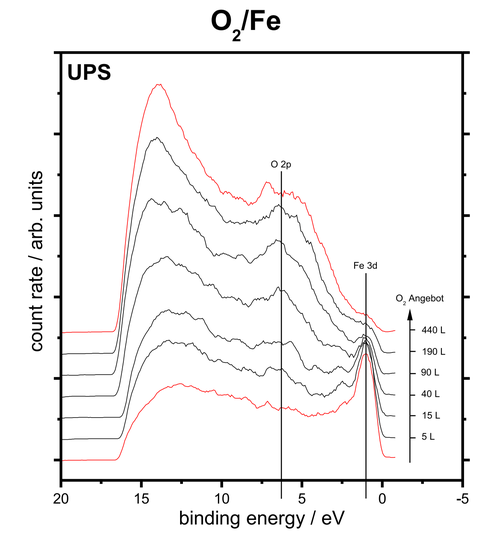
Above XP detail spectra of the Fe2p and O1s are shown.

- Energetic distance Fe^0 ⇔ Fe^{3+}: 4.36 eV
- Energetic distance Fe^{3+} ⇔ Fe^{3+} satellite: 6.76 eV (literature[6],[7],[8]: 8 eV)
- FWHM Fe^0: 2.27 eV (fix parameter, see results for clean iron films)
- FWHM Fe^{3+}: 5.39 eV (literature[6],[7],[8]: 4.5 - 5.0 eV)
- Stoichiometry: O1s ***I*** 64,89 at-%
  Fe2p3/2 ***Fe^{3+}*** 35,11 at-%
  O : Fe ratio ⇨1.85
- ideal O : Fe ratio ⇨ 1.50 for stoichiometric Fe_2O_3
- all parameters listed above and the position of the O1s I account for Fe_2O_3

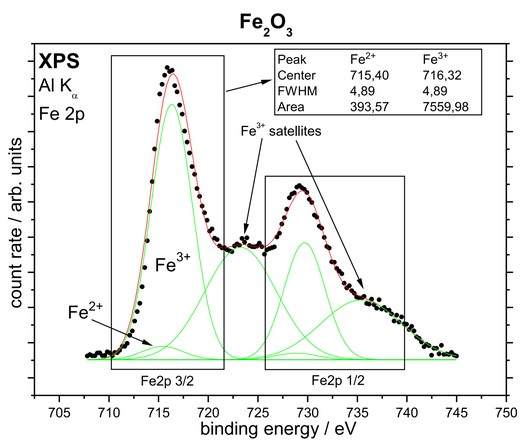
Below MIE and UP spectra are displayed.

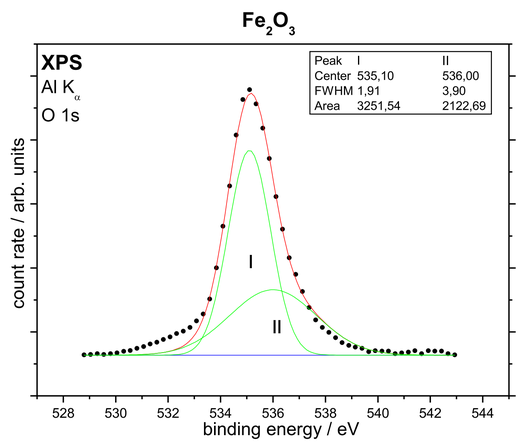
- For MIES the first spectrum shows an RT+AN process typical for a metal; due to oxygen offer, the percentage of secondary electrons rises, but no process change is observed as expected for an insulator
- The UP spectra show the progression of the Fe metal oxidation as found in the literature
- Together all data show the formation of Fe_2O_3





Fe_2O_3 powder



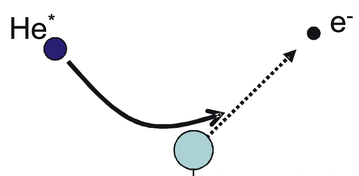


The XP detail spectra for a powder probe are shown above. Fit parameters and stoichiometry indicate a Fe_2O_3:

- FWHM Fe^{3+}: 4.89 eV; FWHM Fe^{2+}: 4.89 eV
- energetic distance between Fe^{2+} and Fe^{3+}: 0.92 eV (literature[6],[7],[8]: approx. 1 eV)
- energetic distance between Fe^{3+} and its satellite: 6.93 eV
- stoichiometry: O1s ***I*** 63,16 at-%
  Fe2p3/2 ***Fe^{3+}*** 36,84 at-%
  O : Fe ratio ⇨1.71

Acknowledgements

We are thankful for the technical assistance of Denise Rehwagen and Christiane Lehmann.



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