Supplementary information for:

Structure, Magnetism, and the Interaction of Water with Ti-Doped Fe₃O₄ Surfaces

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Figure S1. (a) Survey spectra taken after the water isobar for the (110) orientation of the noted composition. (b) Survey spectra taken before (black) and after (gray) the water isobar do not indicate any change in materials stoichiometry or spurious elements, except for some C and Si which remain similar over the course of experiments, as shown for x=0.25 in the (100) orientation.



Figure S2. Effect of heating on x=0. (a) Fe L-edge XAS measured at RT after heating. (b) XMCD at RT on the as-prepared film (thin, as shown in the main text) compared to at RT after annealing at ~480 °C for 1 hour (thick). The colors in (b) represent the same orientations as that in (a).



Figure S3. Fe L-edge XMCD at RT in vacuum on as-prepared $Fe_{3-x}Ti_xO_4$ (110) film of composition x=0 showing component spectra for d6 Oh (green), d5 Td (blue) and d5 Oh (yellow) used to generate the fit (red) of the XMCD data (black).



Figure S4. Fe 3p of x=0.25 in the (100) orientation, probed in UHV at ~480 °C before (green envelope, thin components) and after (black envelope, thick components) the water isobar. The satellites (light gray) overlap with the Ti 3s at ~62 eV, but are not expected to impact the Fe²⁺ (orange):Fe³⁺ (blue) ratio. Spectra are calibrated to the adventitious carbon binding energy (284.8 eV), Shirley-background subtracted and normalized to the maximum intensity.



Fig S5. C 1s spectra corresponding to the O 1s spectra in **Fig. 5** of the main text at the noted RH. The BE scale was calibrated using the O 1s as an internal reference, matching that at the lowest RH to that in UHV after the isobar. The general features remain unchanged in the C 1s, aside from a small increase in oxidized carbon species at ~289 eV. Some initial C–-O species¹ are present, but remain comparable in raw intensity throughout the isobar. This is consistent with the small increase in CO_x species in the O 1s 2.35 eV higher in BE relative to the bulk, where intensity is normalized to the bulk Ox peak in **Fig. 5**. The intensity ratio of this species in the O 1s to that in the C 1s for x=0.25 (110) at $9x10^{-5}$ % RH is ~2, consistent with the relative sensitivity of O:C at similar incident photon energies on the same beamline.



Figure S6. (a, b) Ratio of the CO_x component relative to the lattice oxide (Ox) intensity, which is proportional to coverage. (b, d) Ratio of the oxidized carbon component in the C 1s to the CO_x feature of the O 1s, which is similar across compositions and relative humidity. Compared in (a, c) are noted compositions in the (110) orientation, and (b, d) noted orientations at the x=0.25 composition.



Figure S7. (a, b) Binding energy (BE) location of the Ox feature relative to the bulk OH BE as a function of relative humidity. The smaller BE offset for the x=0 (110) and x=0.25 (111) film are required for a good fit to the spectra, and are correlated with these surfaces having the highest OH/Ox ratio. However, fixing the BE offset to 1.4 eV does not change the trends in OH/Ox ratio, only the absolute magnitude. (c, d) FWHM of the Ox feature (closed) and OH feature (open). Similar to other reports, the Ox feature decreases in FWHM with RH.¹⁻² The OH FWHM is generally larger and similar across RH. Compared in (a, c) are noted compositions in the (110) orientation, and (b, d) noted orientations at the x=0.25 composition.



Figure S8. The difference in the H_2O_{gas} peak BE relative to that of the bulk oxide for (a) different compositions in the (110) orientation and (b) different orientations for x=0.25. The increase in relative gas phase BE is indicative of a decrease in surface work function or change in surface dipole facilitating the removal of photoelectrons from the surface. The sample was not approached or retracted relative to the analyzer or X-ray beam during measurement of the isobar.

Table S1. Atomic concentration from RBS in $Fe_{(3-x)}Ti_xO_4$, modeling the top 5 nm as the "surface". Using XPS, the Fe/Ti ratio is estimated after the water isobar, measured in UHV. Intensities of the Fe 3p and Ti 2p are corrected by tabulated cross sections,³ an estimate of the different photon fluxes comparing the C 1s at both IPEs, the estimated difference in spectrometer efficiencies at the two KEs obtained by comparing the O 1s (KE of ~70 eV at an IPE of 600 eV) and O 2s (KE of ~470 eV at an IPE of 490 eV) corrected by the flux and cross section, and the IMFPs calculated for Fe₃O₄. Note that the IMFP correction assumes the film composition is uniform (taking into account the ratio of over which 95% of the signal was collected), although RBS and previous depth profiling for the (100) orientation in ref. ⁴ indicates Ti is enriched at the surface. This enrichment would result in the Fe/Ti ratio being lower than expected, as observed.

_	Bulk RBS		Surface RBS		XPS
	Х	Fe/Ti ratio	Х	Fe/Ti ratio	Fe/Ti ratio*
x=0 (110)	0.02	143.33	0.01	225.00	_
x=0.25 (110)	0.25	11.14	0.48	5.21	1.51±0.22
x=0.5 (110)	0.42	6.18	0.69	3.32	1.43±0.21

* Corrected by the difference in flux for the two IPEs, the estimated difference in spectrometer efficiencies at the two KEs, the cross section at the IPE of 490 eV for the Fe 3p and 600 eV for the Ti 2p,³ and the difference in depth leading to 95% of the signal, as obtained from the IMFP calculated for Fe₃O₄.⁵⁻⁶

	Fe ²⁺ /Fe ³⁺		
	Before Heating	After Heating @ 750K	
x=0.00 (100)	0.523	0.724	
x=0.00 (110)	0.541	0.744	
x=0.00 (111)	0.599	0.661	
x=0.25 (100)	0.483	-	
x=0.25 (110)	0.590	-	
x=0.25 (111)	0.299	-	
x=0.50 (100)	0.378	-	
x=0.50 (110)	0.613	-	
x=0.50 (111)	0.128	-	

Table S2. Ratio of Fe^{2+} to Fe^{3+} by XMCD at the Fe L-edge, collected in TEY mode at RT in UHV.

Table S3. Percent contribution of the Fe 3p signal by Fe^{2+} (relative to Fe^{2+} and Fe^{3+} combined) and the %Ti from the core level ratio Ti 2p/(Ti 2p + Fe 3p) for x=0.25. The satellite features in the Fe 3p, which are negligible and overlap with the Ti 3s, are not included in either calculation. The (110) orientation generally has a higher amount of Fe^{2+} and Ti. "Before" the isobar is at ~480 °C in UHV, while "After" the isobar is at RT in UHV.

	$\% Fe^{2+} (3p)$		%Ti	
	Before	After	Before	After
x=0.25 (100)	16	4	65	44
x=0.25 (110)	33	31	67	62
x=0.25 (111)	8	1	33	32

Table S4. Percent contribution of the Fe 3p signal by Fe^{2+} (relative to Fe^{2+} and Fe^{3+} combined) for the (110) orientation. The satellite features in the Fe 3p, which are negligible and overlap with the Ti 3s, are not included in either calculation. "Before" the isobar is at ~480 °C in UHV.

	Before
x=0.0 (110)	23
x=0.25 (110)	33
x=0.5 (110)	30

Table S5. Fe 3p fitting in CasaXPS. Similar Fe^{2+} : Fe^{3+} ratios were obtained with a symmetric peak fitting as well. The satellites overlap with the Ti 3s at ~62 eV, but are not expected to impact the Fe^{2+} : Fe^{3+} ratio.

	Fe ³⁺	Fe ²⁺	Satellite 1	Satellite 2
Line shape	A(0.35,0.4,0)GL(0)	A(0.35,0.4,0)GL(0)	GL(0)	GL(0)
FWHM	0.52,3	0.52,3	0.52, 3.5	0.52, 3.5
Binding energy	>52	54,54.5	>60	>62

Table S6. Fitting parameters for the O 1s spectra in CasaXPS, using a Gaussian line shape.

	Ox	OH	CO _x	H ₂ O _{ads}	H_2O_{gas}
FWHM	<1.4	<1.5^	<2	<2	<1.2
Location	Free	Ox+1.15-1.5	Ox+2.35	Ox+3.3*	>534

^The FWHM was constrained only to be less than 1.5, but the fitted values ranged from 1.25-1.5. *Location on an absolute energy scale is \sim 534 eV, similar to other reports in literature.^{2, 4, 7-8}

Table S7. Change in surface speciation and valence for x=0.25 films in the noted orientation. Given is the difference in OH (Δ OH) and the ratio of Fe²⁺/(Fe²⁺+Fe³⁺) from the Fe 3p spectrum (Δ Fe²⁺) measured in UHV before (hot) and after (RT).

	ΔOH	ΔFe^{2+}
x=0.25 (100)	0.26	0.13
x=0.25 (110)	0.13	0.02
x=0.25 (111)	0.09	0.08

Table S8. Change in surface speciation and valence for films in the (110) orientation. Given is the difference in OH (Δ OH) and the ratio of Fe²⁺/(Fe²⁺+Fe³⁺) from the Fe 3p spectrum (Δ Fe²⁺) measured in UHV before (hot) and after (RT).

	ΔOH	ΔFe^{2+}
x=0 (110)	0.49	0.03
x=0.25 (110)	0.13	0.02
x=0.5 (110)	0.14	0.09

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