Surface Chemistry of Almandine Garnet

Jeffrey Poon[1], *David C. Madden*[1], *Mary H. Wood*[1#], *Ron van Tol*[2], *Hans Sonke*[2], *and Stuart M. Clarke**[1]

[1] BP Institute and Department of Chemistry, University of Cambridge, Cambridge UK, CB3 0EZ

[2] Shell Global Research Centre, Amsterdam, The Netherlands

[#] Present address: School of Chemistry, University of Birmingham, Birmingham, B15 2TT

* Corresponding author: stuart@bpi.cam.ac.uk; +00 44 (0) 1223 765700

Supporting Information

Table S1: Quoted Composition of the Almandine Garnet ('Garnet') Abrasive

Mineral Name	Formula	Percentage Composition
Almandine garnet	$Fe_3Al_2(SiO_4)_3$	> 97%
Ilmenite	$FeTiO_3$	< 1.5%
Calcium Carbonate	$CaCO_3$	< 1.5 %
Zircon	$ZrSiO_4$	< 0.2 %
Quartz	SiO_2	< 0.5 %

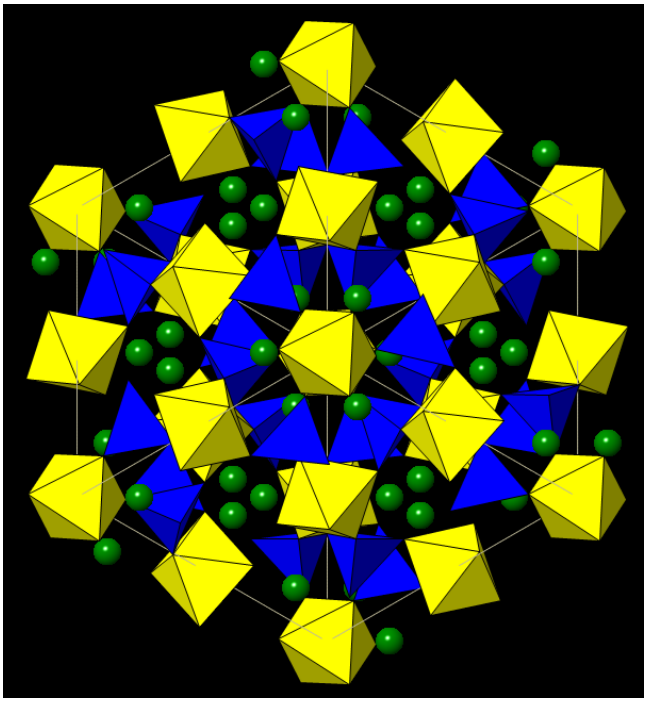


Figure S1: A unit cell of the almandine garnet crystal structure in polyhedral representation. Yellow octahedra are {AlO_6} units, and blue tetrahedra are {SiO_4} units. Green atoms are Fe, residing in large 'voids' within the octahedral-tetrahedral framework.

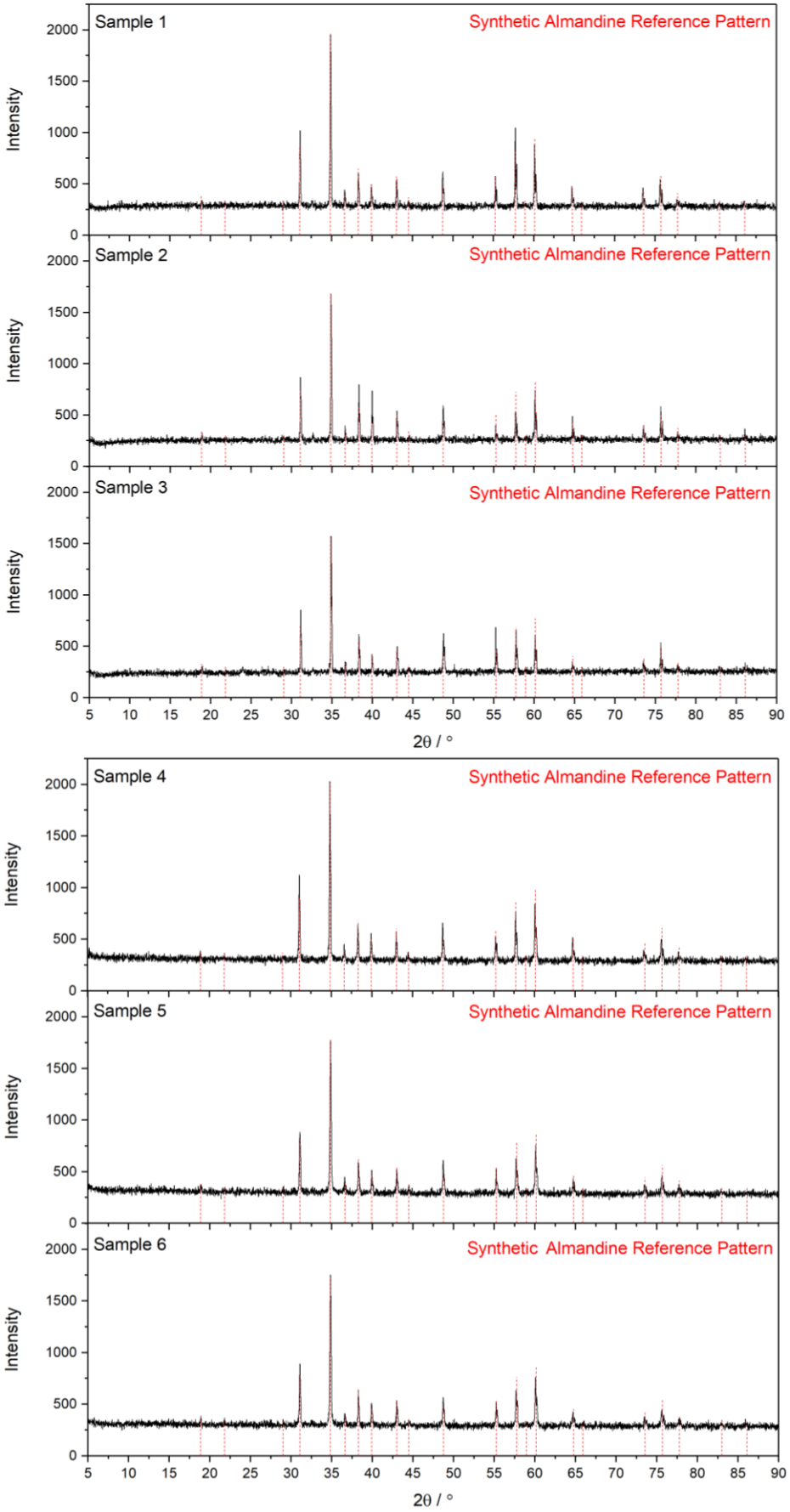
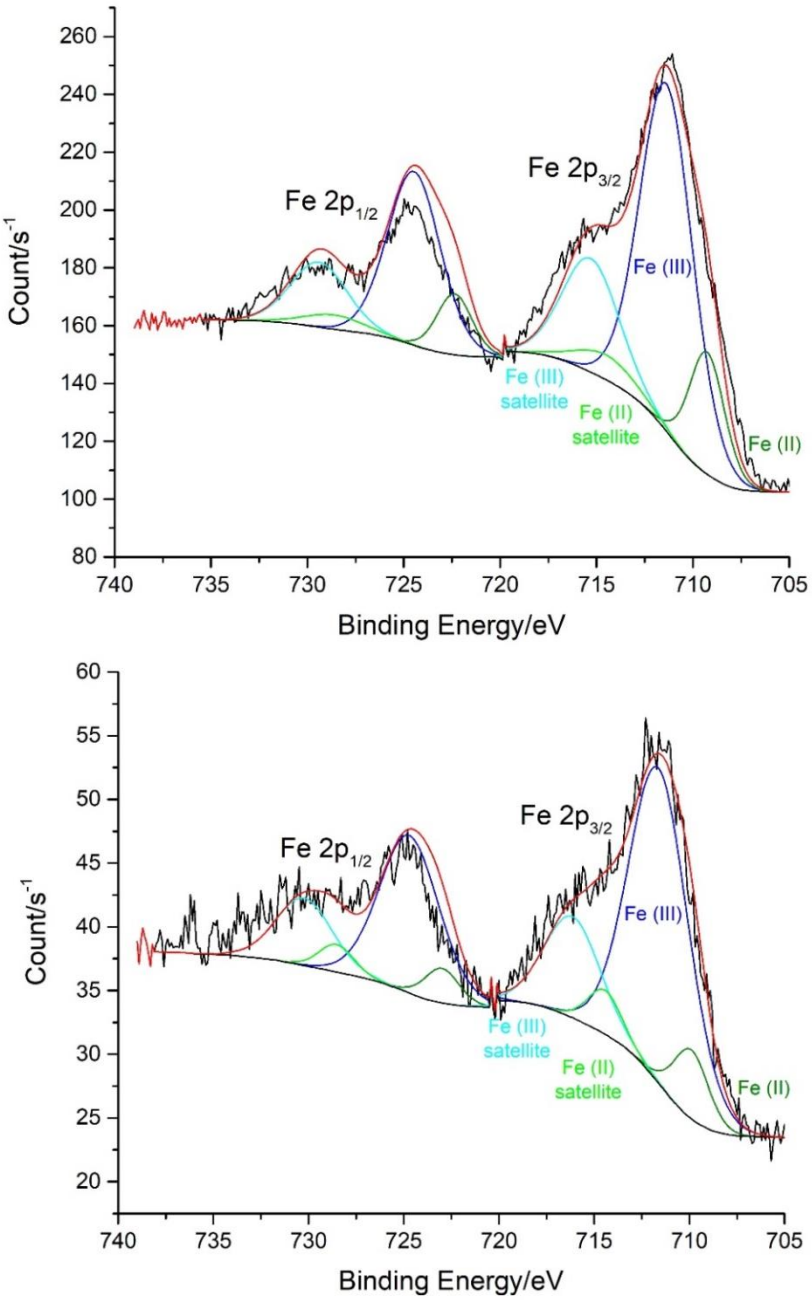


Figure S2: Powder X-ray diffraction data of almandine garnet before (samples 1-3) and after (samples 4-6) acid washing. The powders were tumbled for one week in 0.1 M HCl (samples 1 and 4), ultrapure water (samples 2 and 5) or 0.1 M NaOH (samples 3 and 6); all show good agreement with the reference

almandine garnet spectrum (from American Mineralogist (1992) 77 (5-6) 512-521)), the peaks from which are indicated by the red dotted lines.



Fe 2p		Fe (II)		Fe (III)	
		2p$_{3/2}$	**2p$_{1/2}$**	**2p$_{3/2}$**	**2p$_{1/2}$**
Position / eV		709.27	722.37	711.37	724.47
Full Width Half Maximum / eV	**22.5°**	2.14	2.14	3.23	3.23
	77.5°	2.14	2.14	3.70	3.70
% Area	**22.5°**	19		81	
	77.5°	14		86	

Figure S3: AR-XP spectra for the Fe 2p region at 0° (top) and 50° (bottom) surveying angles to the surface normal, varied by stage tilt, and the corresponding peak fitting results.

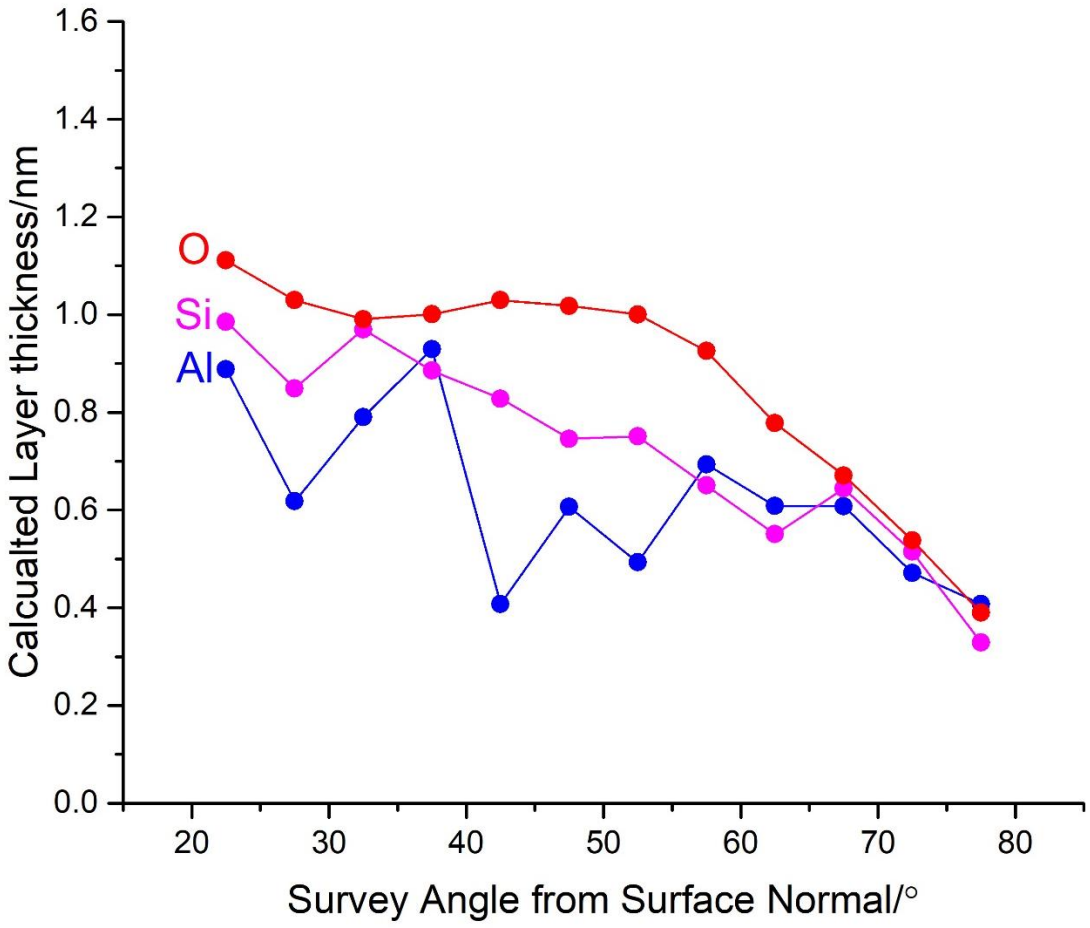


Figure S4: Surface layer thicknesses calculated from AR-XP spectra at different surveying angles for Al, Si and O, using the method discussed in the main text.

Table S2: ICP-OES Results Indicating the Dissolved Fe, Al, and Si in the Supernatant after Tumbling 4 g Acid-Washed Garnet Powder in 20 mL of the Liquid Indicated for One Week (the solids removed were studied with PXRD: these are samples 4-6, shown in Figure S2)

The dissolved concentrations are also converted to estimate the percentage of the atoms initially present in the garnet powder that are dissolved, and the numbers of atoms dissolved per unit area of the solid surface (using the measured specific surface area of the acid-washed garnet powder, 5.54 $m^2 g^{-1}$).

	dissolved concentration / mM			**% of atoms initially present dissolved**			**dissolved atoms from surface / nm^{-2}**		
	Fe	**Al**	**Si**	**Fe**	**Al**	**Si**	**Fe**	**Al**	**Si**
0.1 M HCl	4.161	4.050	4.840	0.3452	0.5040	0.4016	2.262	2.201	2.631
ultrapure water	0.005	0.004	0.627	0.0004	0.0006	0.0521	0.003	0.002	0.341
0.1 M NaOH	0.018	0.608	17.846	0.0015	0.0757	1.4805	0.010	0.330	9.699

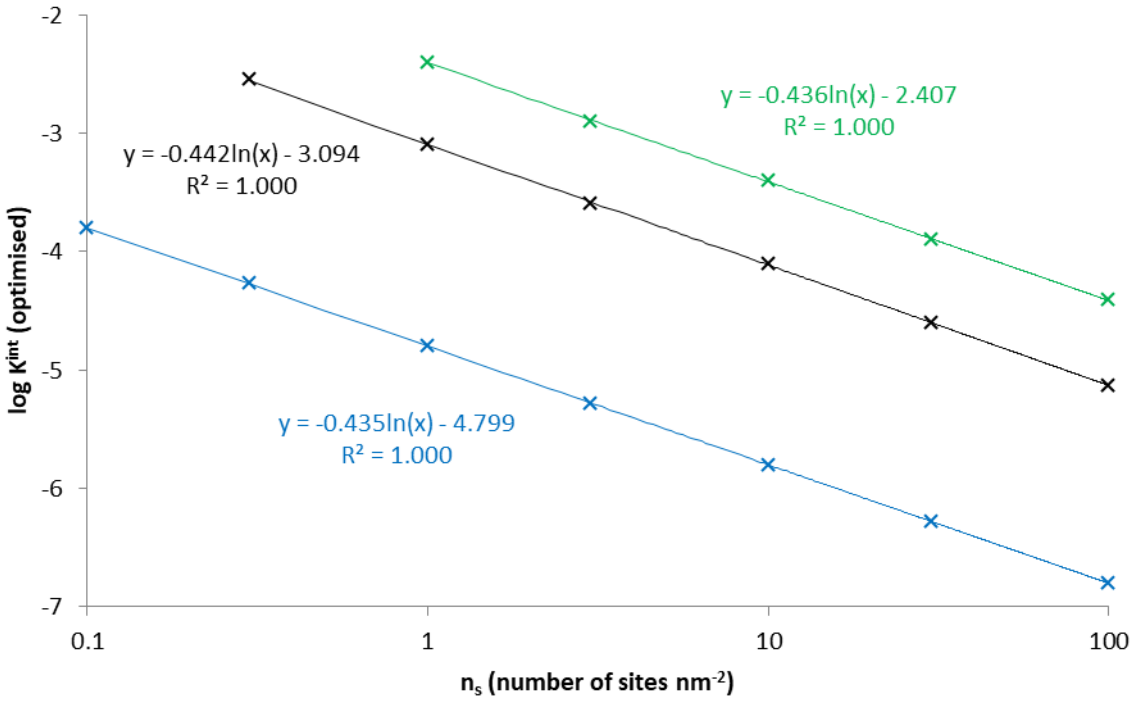


Figure S5: A graph showing the different site densities (n_s) used to fit the experimental salt-solution titration data with numerical modelling for Na (blue), Mg (black) or Ca (green) and ($\log_{10}$ of) the equilibrium constant (K^{int}) that provides the best fit in each case. The linear relationships observed in this log-log plot lead to Equation 10.