

Electronic Supplementary Information:

Effect of Nanosized and Surface-Structural-Modified Nano-Pyroxene on Adsorption of Violanthrone-79

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Table S1. Synthesis conditions for different-sized nano-pyroxene.

Gel	Particle sizes (nm)	Molar ratios of components	Temperature (°C)	Time (h)	Seeding (g)	Calcination (°C, h)
1	10	13.91 Na ₂ O : 9.7 SiO ₂ : Fe ₂ O ₃ : 305 H ₂ O : 6.83 H ₂ SO ₄	160	72	No	No
2	21	11.6 Na ₂ O : 6.9 SiO ₂ : Fe ₂ O ₃ : 290 H ₂ O : 4.5 H ₂ SO ₄	220	24	No	No
3	34	9.1 Na ₂ O : 5.02 SiO ₂ : Fe ₂ O ₃ : 275 H ₂ O : 4.7 H ₂ SO ₄	220	72	No	No
4	45	8.2 Na ₂ O : 4.02 SiO ₂ : Fe ₂ O ₃ : 275 H ₂ O : 4.7 H ₂ SO ₄	250	96	Yes with PY-34	No
5	54	8.2 Na ₂ O : 4.02 SiO ₂ : Fe ₂ O ₃ : 290 H ₂ O : 4.6 H ₂ SO ₄	250	72	Yes with PY-45	No
6	62	8.2 Na ₂ O : 4.02 SiO ₂ : Fe ₂ O ₃ : 275 H ₂ O : 4.7 H ₂ SO ₄	250	96	Yes with PY-45	Yes (850, 3)
7	99	13.91 Na ₂ O : 9.7 SiO ₂ : Fe ₂ O ₃ : 305 H ₂ O : 6.83 H ₂ SO ₄	160	72	No	Yes (800, 2)

Table S2. Synthesis conditions for functionalized nano-pyroxene.

Family	Molar ratio of components	Compound used	Ratio^x Liquid/Solid	Method	Calcination (°C, h)
PY-Ni	-	Ni(NO ₃) ₂ .6H ₂ O	0.78	Wetting impregnation	450, 3
PY -Ca	-	Ca(NO ₃) ₂ .4H ₂ O	20	Ion exchange	-
PY-H	-	H ₂ SO ₄	20	Ion exchange	-
PY-Ce	10.51 Na ₂ O : 4.44 SiO ₂ : 0.18 CeO ₂ : Fe ₂ O ₃ : 321.52 H ₂ O : 5.47 H ₂ SO ₄	Ce(NO ₃) ₃ .6H ₂ O	-	Doping	-
PY-Zr	9.19 Na ₂ O : 3.43 SiO ₂ : 0.15 ZrO ₂ : Fe ₂ O ₃ : 290.57 H ₂ O : 4.9 H ₂ SO ₄	ZrOCl ₂ .8H ₂ O	-	Doping	-

Table S3. Nominal atomic ratios of nano-pyroxene.

Ratio	Si/Fe	Si/Na	Na/Fe	O/Si
PY	2	2	1	3

S1. Computational modeling

S1.1 VO-79 molecule

VO-79 molecule was built with BIOVIA Materials Studio builder module and optimized with BIOVIA Forcite module. The quality of the Geometry Optimization in BIOVIA Forcite was set to Fine: energy: 1.0×10^{-4} kcal/mol; max force: 5.0×10^{-3} kcal/mol/Å; max displacement: 5.0×10^{-5} Å, and using the smart algorithm with the BIOVIA COMPASS Forcefield. The optimized VO-79 molecule is presented in Figure 1b, where an almost flat configuration of the molecule can be noticed with one alkyl chain going out of the paper plane and the other one going down the paper plane.

S1.2 Aegirine structure and surfaces

In order to get an atomistic understanding of the aegirine structure after isomorphous substitution of Si and Fe by Zr and Ce, respectively, as well as its ion exchange to replace the Na^+ in the surface by H^+ and Ca^{2+} , optimization of the aegirine structure was carried out first, then with the optimized structure (shown in Figure 1c), isomorphous replacement of part of the Si and Fe was carried out. Finally, a set of possible surfaces replacing Na^+ by H^+ or Ca^{2+} were generated and optimized. The optimized (001) surfaces are shown in Figure 9 in the accompanying manuscript. The General Utility Lattice Program, GULP^{1,2} was used for all the calculations performed in this part of the study.

This type of calculation is based on lattice energy minimization using interatomic potentials which allows the simultaneous relaxation of the cell constants and the internal coordinates of the

structure. Inorganic, ionic and semionic crystal structures can be modeled by considering two-body ionic short range interaction potentials of the Buckingham type plus an Electrostatic Coulombic interaction term which is evaluated by the Ewald method.³ This form is composed of a Born–Mayer repulsive exponential term and a r^{-6} attractive term:

$$E_{ij} = A_{ij} \exp\left(-\frac{r_{ij}}{\rho_{ij}}\right) - \frac{C_{ij}}{r_{ij}^6} + \frac{q_i q_j}{r_{ij}} \quad (\text{Eq. 1})$$

where r_{ij} is the distance between ions i and j , with charges q_i and q_j , and A_{ij} , ρ_{ij} and C_{ij} are fitted parameters which for the present study are described in Table S9.

For the present work, we have used the well-known interatomic potential developed for silicates by Sanders et al,⁴ and for the sodium the potentials reported by Bush et al.⁵ The tetrahedral and octahedral configurations of oxygen atoms around silicon and iron atoms are better represented if we introduce a harmonic three-body short-range interaction potential for each one to simulate the covalent effects. This three-body potential is of the type

$$E_{ijk} = \frac{1}{2} K_{ijk} (\Theta - \Theta_0)^2 \quad (\text{Eq. 2})$$

It is a simple harmonic potential about the equilibrium bond angle, where K_{ijk} is the force constant and $(\Theta - \Theta_0)$ is the deviation from the equilibrium angle, which is 109.47° and 90° respectively for the ideal tetrahedral and octahedral angles and, the values were taken from Winkler et al,⁶ and Sainz-Diaz et al.⁷

The electronic polarizability of the ions is taken into account by using the classical model of Dick and Overhauser.⁸ According to this polarizable ion model, the oxygen ions in the present case are represented by a core and a massless shell, connected by a spring. The electronic

polarizability of the model ion, EP , is then determined by the spring constant and the charges of the core and shell:

$$EP = \frac{1}{2}Kr^2 \quad (\text{Eq. 3})$$

where r is the separation distance between the centers of the core and the shell. In this work the core is assigned a charge of $+0.86902e$ and the shell a charge of $-2.86902e$,⁴ maintaining the formal value for the overall ionic charge as -2 . During the energy minimization calculations, the shell positions are allowed to relax about the ionic core resulting in a dipole that mimics the electronic polarization. In this model, all intermolecular potentials act on the shell of the atom if one exists or on the core if one does not.

The O and H atoms within the hydroxyl group are given non-formal charge values ($H_{(\text{OH})} = +0.426e$ and $O_{(\text{OH})} = -1.426e$),⁷ although the overall charge on the hydroxyl ion has a formal charge of -1 . The intramolecular OH interaction is described by a Morse potential:

$$E = D\{1 - \exp[-a(r - \mu)]\}^2 \quad (\text{Eq. 4})$$

where r and μ are the observed and equilibrium interatomic distances, respectively. The parameters D and a are described in Table S9.⁷ The interatomic potentials for iron in the pyroxene Aegirine were obtained by applying the relax fitting procedure within the GULP program. The structural parameters of Aegirine reported by Cameron et al,⁹ and the elastic constants reported by Aleksandrov et al,¹⁰ were used in the fitting. The obtained values are reported in Table S9.

To get an insight in the surface of the Aegirine materials, the program GTK Display Interface for Structures (GDIS)¹¹ was used to draw several possible surfaces and to produce the input files for the program GULP. All construction of the surface and structural manipulation were performed

independently from the main forcefield engine (GULP) by graphical means. This was achieved through the interface of the freely available program GDIS.¹¹ This interface allowed surfaces to be specified by their Miller indices, valid shifts to be searched for and the geometries then to be manipulated, for instance, replacing the surface sodium ions by Ca, H⁺, etc. Once the desired surface structure has been generated, then the necessary GULP calculation was performed.

Table S4. Potential parameters used in the present calculations.

Charges (e)			
Ions	Core	Shell	
Si	+4.00000		
Na	+1.00000		
Fe	+3.00000		
O	+0.86902	-2.86902	
Ce	+3.00000		
Zr	+4.00000		
Ca	+2.00000		
O _(OH)	-1.42600		
H _(OH)	+0.42600		
Buckingham			
Interaction ^a	<i>A</i> (eV)	ρ (Å)	<i>C</i> (eV Å ⁻⁶)
Si _{core} - O _{shell}	1283.9070	0.320500	10.6616
Na _{core} - O _{shell}	1271.5040	0.300000	0.0
Fe _{core} - O _{shell}	661.80121	0.366356	0.0
Ce _{core} - O _{shell}	1731.6200	0.363700	14.4300
Zr _{core} - O _{shell}	1453.8000	0.350000	0.0
Ca _{core} - O _{shell}	874.68065	0.346346	0.0
O _{shell} - O _{shell}	22764.000	0.149000	27.8800
Si _{core} - O _(OH)	983.55700	0.320500	10.6616
Fe _{core} - O _(OH)	862.08000	0.329900	0.00000
H _(OH) - O _{shell}	325.00000	0.250000	0.00000
Morse potential	<i>D</i> (eV)	<i>a</i> (Å ⁻¹)	μ (Å)
	7.0525	2.1986	0.9485

Spring Interaction	K (eV Å ⁻²)	
O _{core} - O _{shell}	74.92000	
Three-body Interaction	k_{θ} (eV rad ⁻²)	θ (degrees)
O _{shell} - Si _{core} - O _{shell}	2.0972	109.47
O _{shell} - Fe _{core} - O _{shell}	2.0972	90.00
O _{shell} - Ce _{core} - O _{shell}	2.0972	90.00
O _{shell} - Zr _{core} - O _{shell}	2.0972	109.47

^aThe cutoff distance for the Buckingham potential was 12 Å

The surfaces consisted of two regions that are periodic in two dimensions. Atoms in region I contain the surface layers and are allowed to relax to mechanical equilibrium. Region II contains atoms that are further away from the surface into the bulk. These are kept fix at their bulk equilibrium position and represent the crystal continuum. The two regions, I and II, are ensured to be sufficiently large for the total energy to converge. The surfaces were then optimized using the program GULP in which the atoms of region I were allowed to relax, and the atoms in region II (representing the bulk) were fixed. The depth of each region was between 12 and 16 Å.

Table S10 and S11 show the comparison of the structural and elastic constant values obtained for aegirine, using the interatomic potentials described in Table S9, with the reported experimental values of those parameters. As it can be seen, the agreement is good between the reported values for aegirine and the calculated ones. Also, the partial replacement of Ce and Zr in the structure produces an increase in the cell parameters as expected (Table 3 in the accompanying manuscript).

Table S5. Comparison of structural values obtained by the optimization procedure with GULP with those experimentally reported for aegirine.

Parameter	NaFeSi ₂ O ₆ *Cameron et al. ⁹	NaFeSi ₂ O ₆ This work	NaFe _{0.92} Ce _{0.08} Si ₂ O ₆ This work	NaFeSi _{1.87} Zr _{0.13} O ₆ This work
a (Å)	9.658(2)	9.705	9.776	9.825
b (Å)	8.795(2)	8.772	8.935	8.775
c (Å)	5.294(1)	5.297	5.329	5.371

β (°)	107.42(2)	106.29	105.77	106.54
V (Å ³)	429.1(1)	432.8	448.0	443.9

*values in parenthesis are the reported standard deviation.

Table S6. Elastic stiffness coefficients (in GPa) for aegirine as calculated in this work with the interatomic potentials and their comparison with experimental data.^{10,12}

Stiffness coefficient	Aleksandrov et al. ¹⁰	This work
C11	185.8	169.7
C22	181.3	166.4
C33	234.4	279.9
C44	69.2	62.1
C55	51.0	42.3
C66	47.4	56.2
C12	68.5	75.7
C13	70.7	82.2
C23	62.6	96.1
C15	9.8	19.6
C25	9.4	15.0
C46	7.7	11.3
B*	117	118

*Bulk modulus from reference 12.

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