Surface hydration of pyrochlore mineral: A DFT study of a single water molecule adsorption on low-index surfaces

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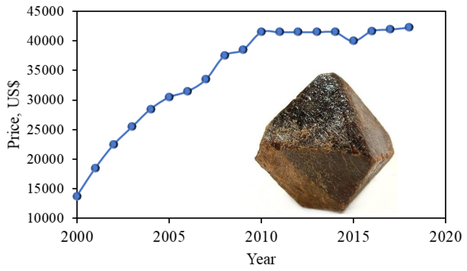
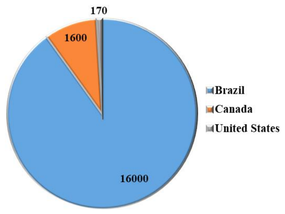
Introduction

Pyrochlore as a strategic Nb mineral:

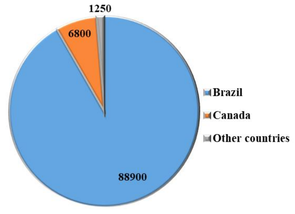
- Pyrochlore ($Ca_2Nb_2O_6F$): major niobium-containing mineral.
- Niobec mine (Canada), a major producer.
- Nb price has been increased since 2000.



Price of Nb metal from 2000 to 2018



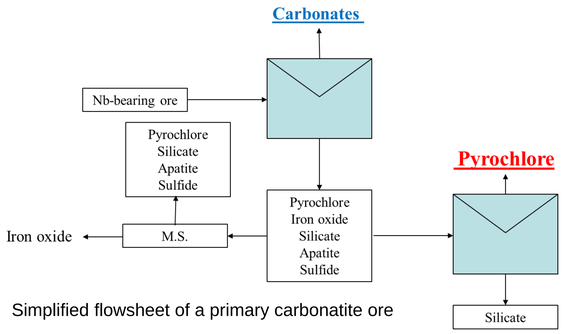
Global reserves data (kt) of Nb in 2019



Global mine production (t/y) of Nb in 2019

Pyrochlore Processing:

- Froth flotation is the main processing method for Nb-bearing minerals.
- In-direct flotation is compatible with the ore geology of Niobec mine.
- Carbonate minerals are first floated using fatty acid collectors in alkaline pH.
- Pyrochlore is then floated using amine collectors.



Simplified flowsheet of a primary carbonatite ore

Surface Hydration:

- Surface hydration is the adsorption of water molecules on mineral surfaces.
- The chemical reagents adsorb on hydrated mineral surfaces.

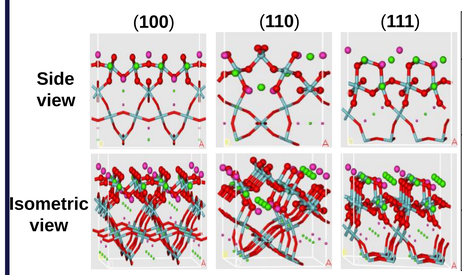
METHODOLOGY

Geometry optimization:

- DMol3 was employed for geometry optimization and energy calculation of pyrochlore low-index surfaces.
- Grand canonical Monte Carlo approach, evaluation of the different absorbate initial sites.
- The Fukui function, Hirshfeld population charge, bond population, and partial density of states were employed to determine active sites, bond nature, and explain the electronic structure.

RESULTS

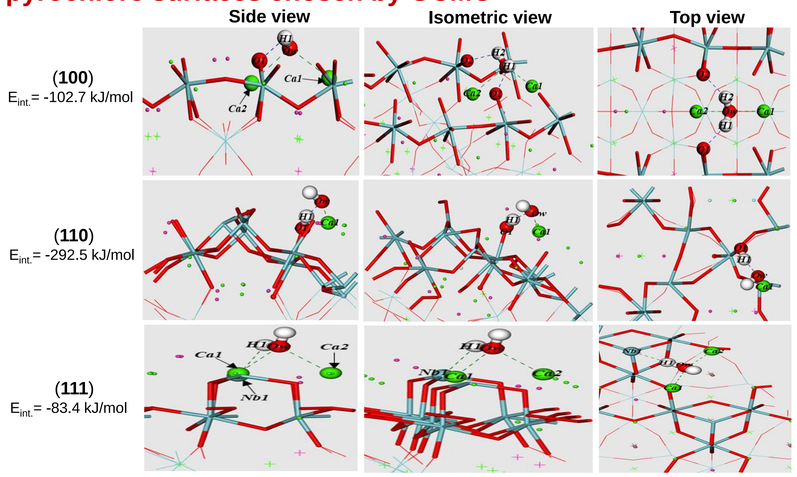
Geometry optimization and reactivity of surface atoms



The value of Fukui indices for the surface atoms on $Ca_2Nb_2O_6F$ (100), (110), and (111) surfaces

Surface	Atom label	Fukui indices f^+	Fukui indices f^-	Hirshfeld charge value
100	Nb	0.01		0.6937
	Ca	0.008		0.4163
	O (-)		0.014	-0.2471
	O (=)		0.006	-0.2771
	F		0.013	-0.1885
110	Nb	0.035		0.6064
	Ca	0.027		0.4452
	O (=)		0.018	-0.3524
	O (-)		0.013	-0.3317
	F		0.007	-0.2166
111	Nb	0.029		0.3511
	Ca	0.024		0.3255
	O		0.001	-0.3424
	F		0.008	-0.2449

The most energetically favorable structures of low-index pyrochlore surfaces chosen by GCMC

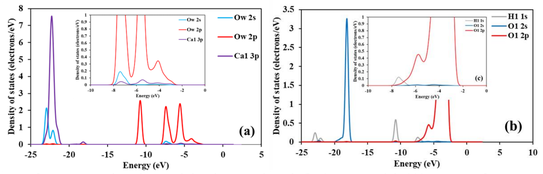


Characterization of the covalent, van der Waals, and hydrogen bonding, of a single water molecule on the $Ca_2Nb_2O_6F$ low-index surfaces

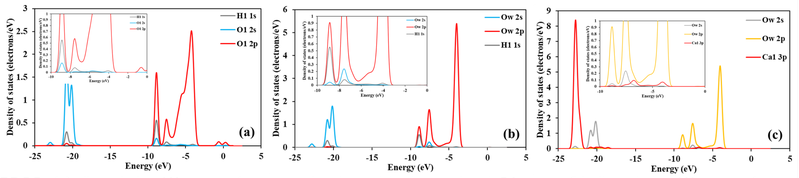
Surface	Covalent/vdW bonds: Bond	Bond population	(Atom) charge before adsorption	(Atom) charge after adsorption	H bonds: H bond	Bond population	O charge before adsorption	O charge after adsorption
100	Ca1-Ow	0.05	0.4163 (Ca1)	0.4182 (Ca1)	H1-O1	0.01	-0.2470	-0.2667
	Ca2-Ow	0.03	0.4163 (Ca2)	0.3890 (Ca2)	H2-O2	0.01	-0.2470	-0.2665
110	Ca1-Ow	0.23	0.4452 (Ca1)	0.4141 (Ca1)	H1-Ow	0.12	-0.3090	-0.2666
	H1-O1	0.56	-0.3317 (O1)	-0.2718 (O1)				
111	Ca1-Ow	0.09	0.3255 (Ca1)	0.3309 (Ca1)	-	-	-	-
	Ca2-Ow	0.09	0.3251 (Ca2)	0.3318 (Ca2)				
	Nb1-H1	0.04	0.3511 (Nb1)	0.3566 (Nb1)				

RESULTS (CONT'D)

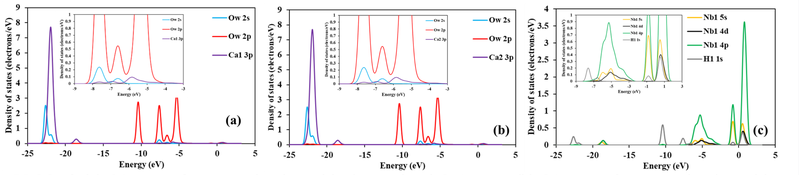
Electronic structure: Partial density of state (PDOS)



PDOS: (a) O atom of water molecule and its interactional Ca1 atom, (c) H1 atom of water molecule and its interactional O1 atom on $Ca_2Nb_2O_6F$ (**100**) after water molecule adsorption.

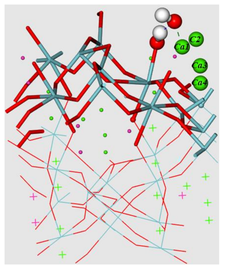


PDOS: (a) dissociative H1 atom of water molecule and its interactional O1 atom, (b) dissociative H1 atom of water molecule and its interactional dissociative O atom of water molecule, (c) O atom of water molecule and its interactional Ca1 atom on $Ca_2Nb_2O_6F$ (**110**)

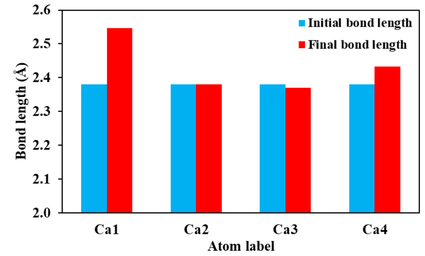


PDOS of: (a) O1 atom of water molecule and its interactional Ca1 atom, (b) O1 atom of water molecule and its interactional Ca2 atom, (c) H1 atom of water molecule and its interactional Nb1 atom on $Ca_2Nb_2O_6F$ (**111**) after water molecule adsorption.

Potential of surface Ca dissolution on pyrochlore (110) surface



Orientation of Ca1 towards dissociated hydroxyl group



Influence of water adsorption on surface structure of $Ca_2Nb_2O_6F$ (**110**).

CONCLUSIONS

- Dissociative water adsorption is more thermodynamically favorable on (110) surface
- Associative water adsorption is the only surface hydration mechanism on (100) and (111) pyrochlore surfaces
- Hydrophilicity: (110)>(100)>(111)
- Pyrochlore surface hydration promotes Ca dissolution

ACKNOWLEDGMENTS

CRSNG NSERC