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A Computational Study on Geochemical Stability of Natural and Engineered Sesquioxide Nanominerals

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INTRODUCTION

Sesquioxide minerals, which follow the generic formula R_2O_3, are widely distributed in both geological and man-made materials. Within the Earth's environment, sesquioxides of iron and chromium, such as hematite (Fe_2O_3) and eskolaite (Cr_2O_3) are important components of soil and crustal mineral assemblages, playing significant roles in geochemical cycling, including metal adsorption, nutrient redistribution, and redox transformations. Beyond these naturally occurring species, engineered sesquioxides such as gallium oxide (Ga_2O_3) and scandium oxide (Sc_2O_3) have gained increasing technological importance in recent years, finding applications in electronics, catalysis, and advanced ceramic materials. Nevertheless, the nanoscale thermodynamic stability of sesquioxide minerals under ambient geochemical conditions remains poorly understood. At the nanoscale, stability can be affected by factors such as structural symmetry, electronic configuration, and molecular polarity, and by how these factors interact with the surrounding environment, including aqueous ions, pH gradients, and redox processes. Experimental probing of such atomic-scale phenomena is often fraught with difficulties, and thus theoretical and computational approaches become invaluable tools for dissecting mineral stability and electronic structure. Quantum-chemical methodology based on Density Functional Theory provides a rigorous framework for searching for structural, thermodynamic, and electronic properties of mineral systems at the atomic level. In the current investigation, the calculations were performed with Gaussian 09W to study the thermodynamic and electronic properties of selected natural and engineered sesquioxide nanominerals. Key thermodynamic parameters, such as internal energy, enthalpy, Gibbs free energy, heat capacity (C_v), and entropy, were calculated in parallel with electronic descriptors, such as dipole moment and point-group symmetry. Representative R_2O_3 systems, including Fe_2O_3, Cr_2O_3, Ga_2O_3, and Sc_2O_3, were studied using a uniform computational protocol. The resulting data show that, although the overall magnitudes of the thermodynamic properties of the investigated sesquioxides remain broadly similar under standard conditions, distinguishable differences occur in electronic structure and dipole behavior depending on the symmetry of the molecule. These findings highlight the value of quantum-chemical calculations in providing detailed information on the nanoscale stability of sesquioxide minerals and their electronic properties.

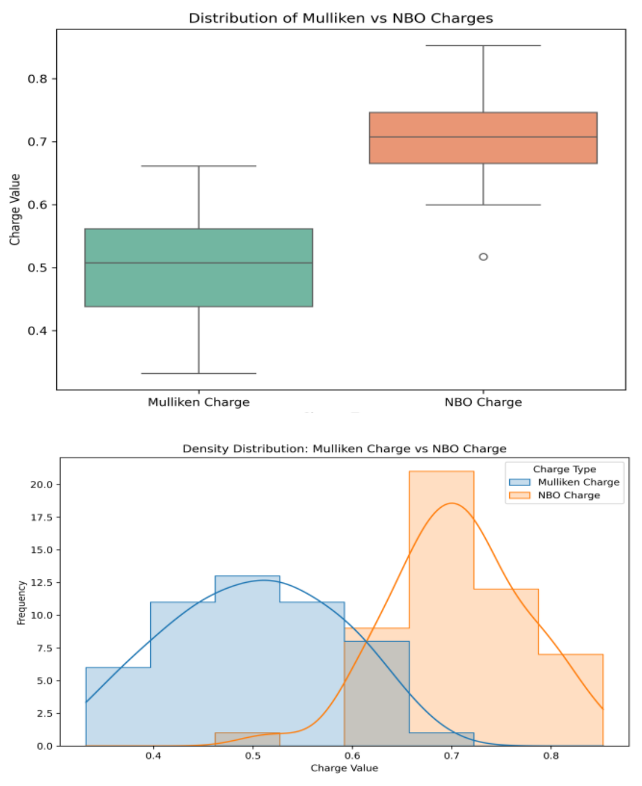
METHODOLOGY

This study investigates the structural, thermodynamic, and electronic properties of selected sesquioxide nanominerals using Density Functional Theory. All the quantum-chemical calculations have been performed using Gaussian 09W with the LANL2DZ basis set, taking into account the effective core potentials of the heavier elements, to describe the electronic configuration of the considered systems. Representative R_2O_3 sesquioxides, that is, Fe_2O_3, Cr_2O_3, Ga_2O_3, and Sc_2O_3, were selected for detailed analysis. Initial molecular geometries were drawn and then optimized to give stable structures, equivalent to minimum-energy structures. Following optimization of the geometry, vibrational frequency calculations were carried out to verify the stability of the optimized structures and to obtain thermodynamic parameters. These parameters, such as internal energy, enthalpy, Gibbs free energy, entropy, constant-volume heat capacity (C_v) etc. have been determined by the frequency analysis. Moreover, electronic descriptors like dipole moment and point group symmetry were calculated to determine the electronic properties and structural stability of the investigated sesquioxide nanominerals. The HOMO–LUMO gap was calculated as the energy difference between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) obtained from the DFT calculations.

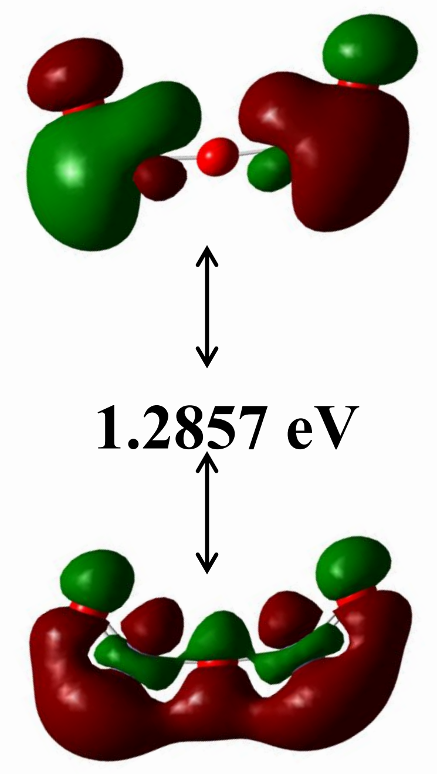
RESULTS & DISCUSSION

Natural Nanominerals:

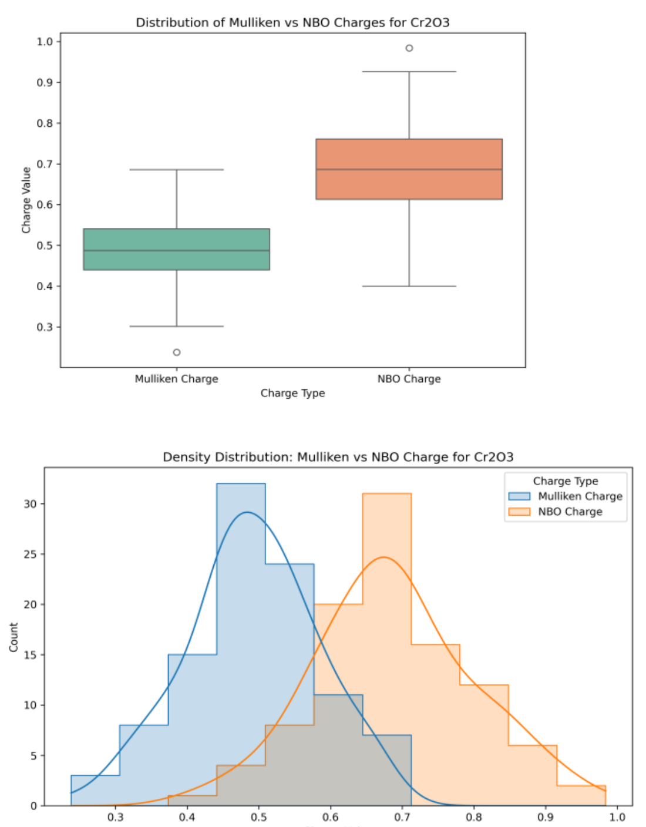
Fe_2O_3 :



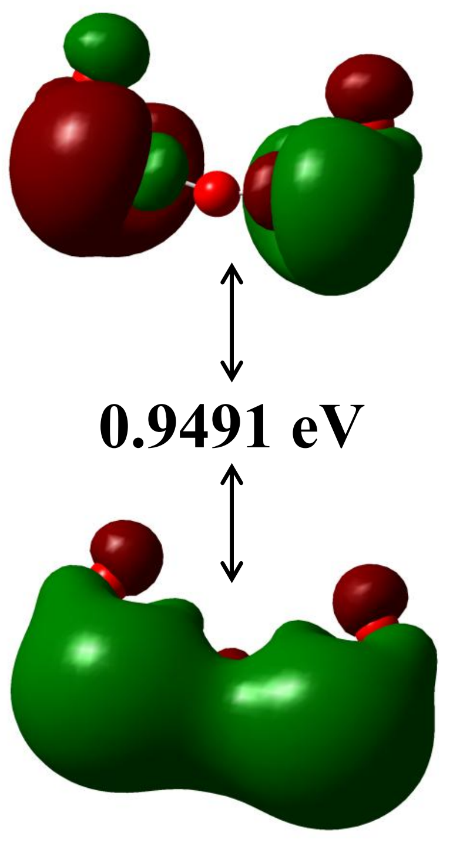
HOMO–LUMO Gap



Cr_2O_3 :

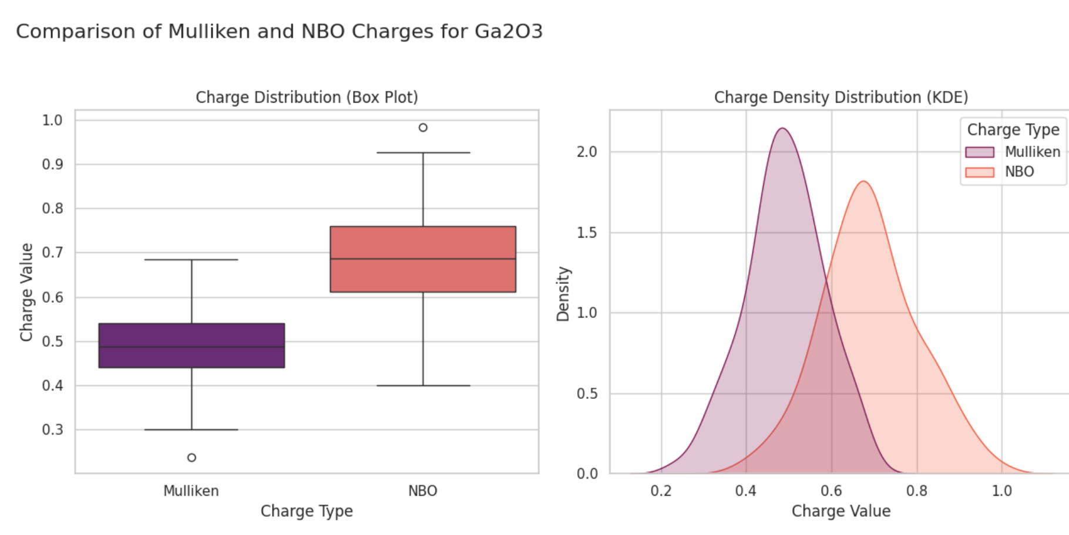


HOMO–LUMO Gap

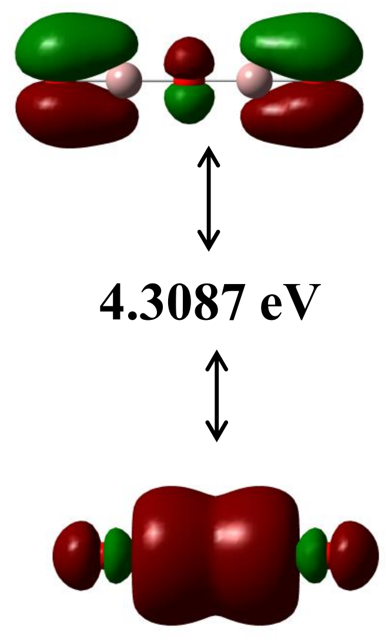


Engineered Nanominerals:

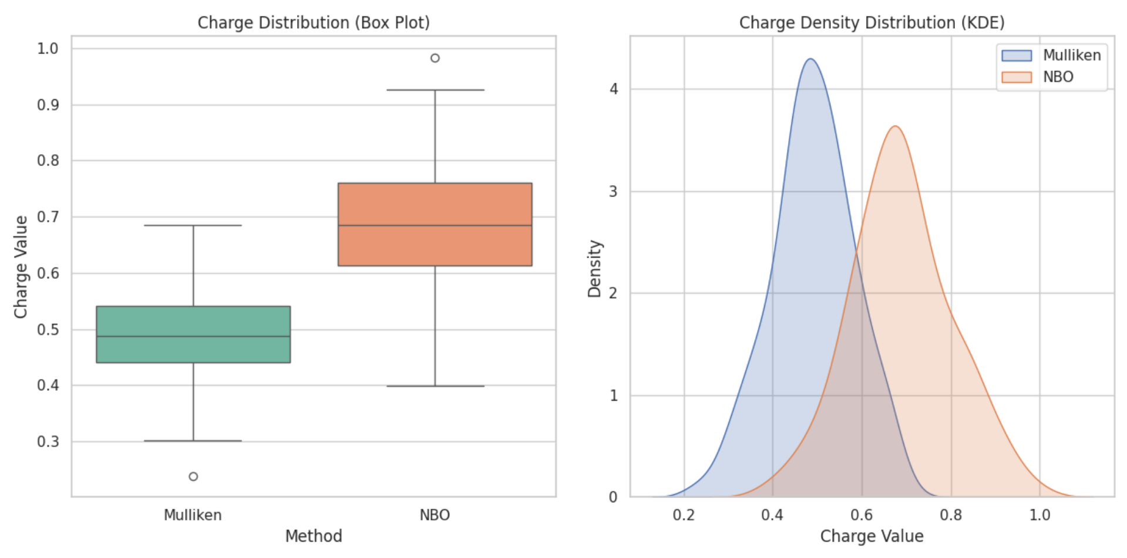
Ga_2O_3 :



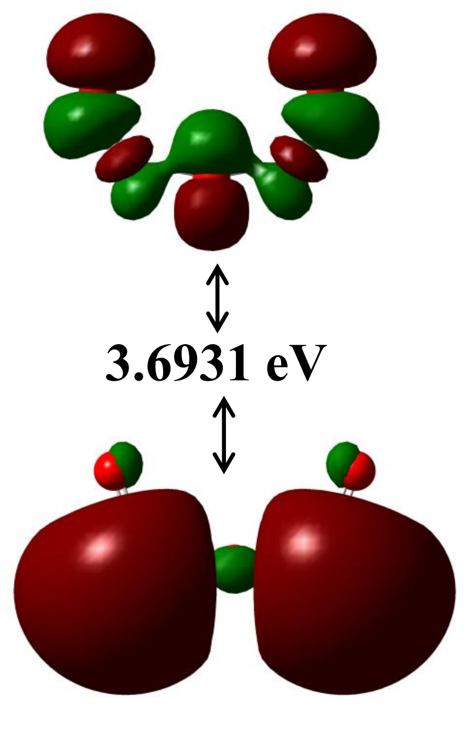
HOMO–LUMO Gap



Sc_2O_3:



HOMO–LUMO Gap



Density functional theory calculations show that the investigated sesquioxide nanominerals exhibit comparable thermodynamic stability but differ in their electronic structure and charge distribution. Natural oxides such as Fe_2O_3 and Cr_2O_3 demonstrate stronger metal–oxygen interactions and more delocalized electronic structures, which are characteristic of minerals commonly found in geochemical environments. Frontier molecular orbital analysis indicates that natural sesquioxides possess smaller HOMO–LUMO separations, suggesting relatively higher electronic reactivity and enhanced charge transfer within the metal–oxygen framework. In contrast, engineered oxides such as Ga_2O_3 and Sc_2O_3 show wider electronic gaps and more localized orbital distributions, indicating greater intrinsic electronic stability. Charge population analyses further reveal noticeable differences between Mulliken and NBO methods, with NBO results predicting stronger charge transfer between metal and oxygen atoms. Variations in dipole behavior and molecular symmetry also highlight differences in charge distribution among the studied systems. Overall, the results suggest that natural sesquioxide nanominerals appear more suitable for geochemical environments due to their favorable electronic reactivity and charge transfer characteristics, while engineered oxides exhibit greater electronic stability. The results suggest that natural sesquioxides may exhibit greater geochemical reactivity due to smaller HOMO–LUMO gaps, whereas engineered oxides demonstrate greater intrinsic electronic stability.

Molecule	Free Energy (KJ/mol)	Internal Energy (KJ/mol)	Zero Point energy (KJ/mol)	RB3LYP Energy (KJ/mol)	Enthalpy (KJ/mol)	Entropy (cal/mol-K)	Dipole Moment (Debye)	Heat Capacity, C_v (cal/mol-K)	Symmetry
Cr_2O_3	-1045473.9031	-1045368.5313	23.3932	-1045409.4245	-1045366.0528	86.455	6.4841	18.300	CS
Fe_2O_3	-1240235.6670	-1240129.2214	22.4428	-1240169.8252	-1240126.7429	87.317	5.1645	18.47	C2V
Ga_2O_3	-603438.1042	-603351.2343	22.7001	-603391.3978	-603348.7532	71.626	0.0028	18.565	CS
O_3Sc_2	-837040.3258	-836941.3077	22.7001	-836979.2937	-836938.8292	81.364	12.2208	16.386	CS

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