



## Data Article

## Dataset on the crystal structure and electronic properties of kaolinite edge surfaces



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## ABSTRACT

The data presented in this paper characterize stable kaolinite edge surfaces. Their equilibrium structure is obtained by DFT methods using the first-principles package CASTEP. The calculations are performed using a basis set of plane waves in the PBE exchange-correlation potential. The dispersion forces are taken into account using the semi-empirical Grimme-D2 correction. For selected kaolinite surfaces: (001),(001), (010), (110) the paper presents their optimized crystal structure, values of terminal hydroxyl groups charges, density of electronic states, and work function. The presented data allow characterizing the stability of the surfaces and giving their comparative evaluation. This set of surfaces can be used for a comparative study of adsorption of atoms, ions and other molecular systems.

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## Specifications Table

Subject	Surfaces and Interfaces
Specific subject area	Surface and Interface Chemistry of Clay Minerals
Data format	Raw, Analyzed
Type of data	Table, Graph, Figure
Data collection	Models of kaolinite edge surfaces (001), (00̄1), (010) and (110) were constructed on the basis of a pre-optimized $2 \times 1 \times 2$ cell by delamination in the direction of the corresponding crystallographic plane. The positions of the delamination planes were chosen to minimize the number of broken bonds. Compensation for broken bonds was accomplished by chemical sorption of H <sub>2</sub> O molecules until a zero total charge model was obtained. The resulting kaolinite surface models were optimized using the first-principles package CASTEP. The calculation was performed in the generalized gradient approximation in the PBE potential. Noncovalent forces were taken into account using the semiempirical Grimme-D2 correction.
Data source location	<ul style="list-style-type: none"> <li>• Institution: Rostov State Transport University</li> <li>• City/Town/Region: Rostov-on-Don</li> <li>• Country: Russia</li> </ul>
Data accessibility	<p>Repository name: Mendeley Data          Data identification number: <a href="https://doi.org/10.17632/f3wvxrxgz.2">10.17632/f3wvxrxgz.2</a>          Direct URL to data: <a href="https://data.mendeley.com/datasets/f3wvxrxgz/2">https://data.mendeley.com/datasets/f3wvxrxgz/2</a>          Instructions for accessing these data: free access</p>

## 1. Value of the Data

- Structural and electronic characteristics of the most stable edge surfaces of kaolinite, such as (001), (00̄1), (010) and (110) are presented.
- The models of kaolinite edge surfaces can be used in the construction of macromodels for the study of interfacial phenomena.
- They can be used for comparative studies of adsorption processes for mineral surfaces of different types.
- Data on the charge value of atoms of surface OH-groups, the densities of electronic states of surface models allow identifying adsorption centers on the basis of changes in these characteristics.

## 2. Background

The dataset presented in this data article originates from an extensive research endeavor dedicated to the study of kaolinite, a mineral well-known for its specific surface attributes that carry significant implications in a wide array of industrial and scientific settings. The edge surfaces of kaolinite were obtained by sectioning the three-dimensional structure along the following crystallographic planes: (001), (00̄1), (010) and (110). The position of the surfaces for mineral dissection was chosen to minimize broken bonds. Chemical sorption of water molecules to neutral total model charge was used to compensate for broken bonds. The optimization of the surface models of kaolinite was carried out through the application of Density Functional Theory (DFT) techniques using the CASTEP software, which integrates the generalized gradient approximation and the PBE potential, in addition to implementing the Grimme-D2 correction to accurately consider dispersion forces in the system. This dataset serves as a valuable addition to the existing body of research by offering in-depth insights into the structural and electronic attributes of kaolinite surfaces, which are instrumental for comparative analyses in adsorption processes on mineral surfaces and the formulation of macroscopic models for interfacial phenomena.

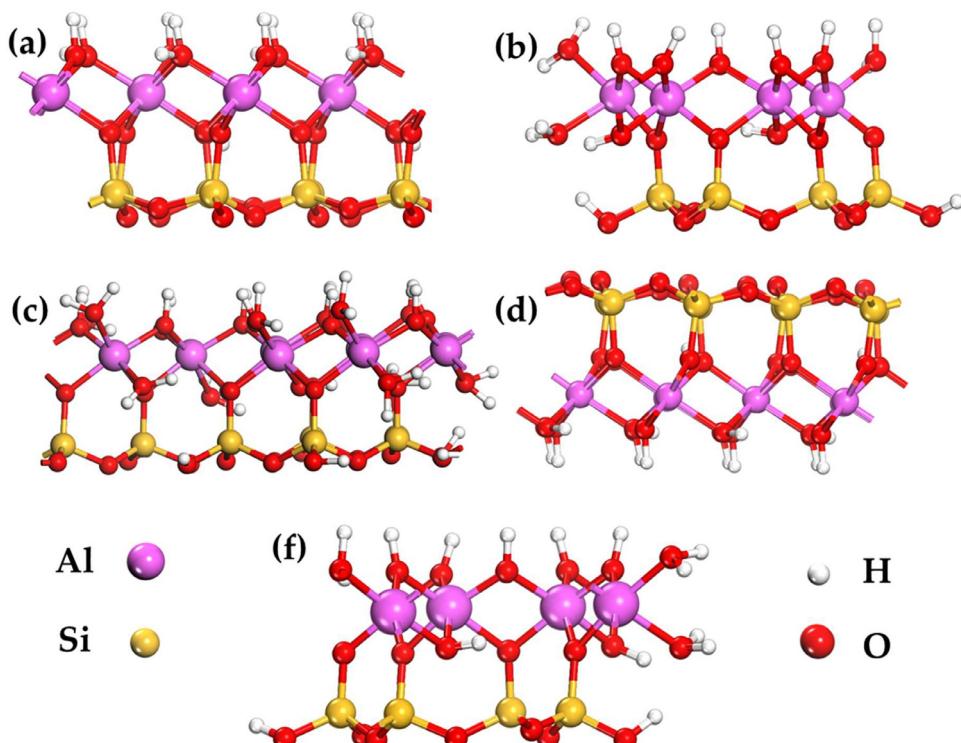
### 3. Data Description

**Fig. 1** shows the stable edge surfaces of kaolinite. They are obtained by sectioning along the crystallographic planes (001), ( $00\bar{1}$ ), (010) and (110) with minimization of broken bonds. For the basal surfaces (001) and ( $00\bar{1}$ ), the crystallographic planes coincide with the cleavage planes (**Fig. 1a,d**). For surface (010), the following terminal groups are obtained: Si-OH and  $\text{H}_2\text{O}-\text{Al}-\text{OH}_2$  (**Fig. 1b**), and Si-OH and Al-OH<sub>2</sub> (**Fig. 1f**). For surface (110), the following type of terminal groups occur: Si-OH,  $\text{H}_2\text{O}-\text{Al}-\text{OH}_2$  and Al-OH<sub>2</sub> (**Fig. 1c**). The given geometrical structures of kaolinite edge surfaces were optimized until an equilibrium state was reached. Dispersion forces were taken into account as a correction to the calculated total energy of the system. Taking into account this correction ensured a correct description of the behavior of end OH-groups of kaolinite edge surfaces.

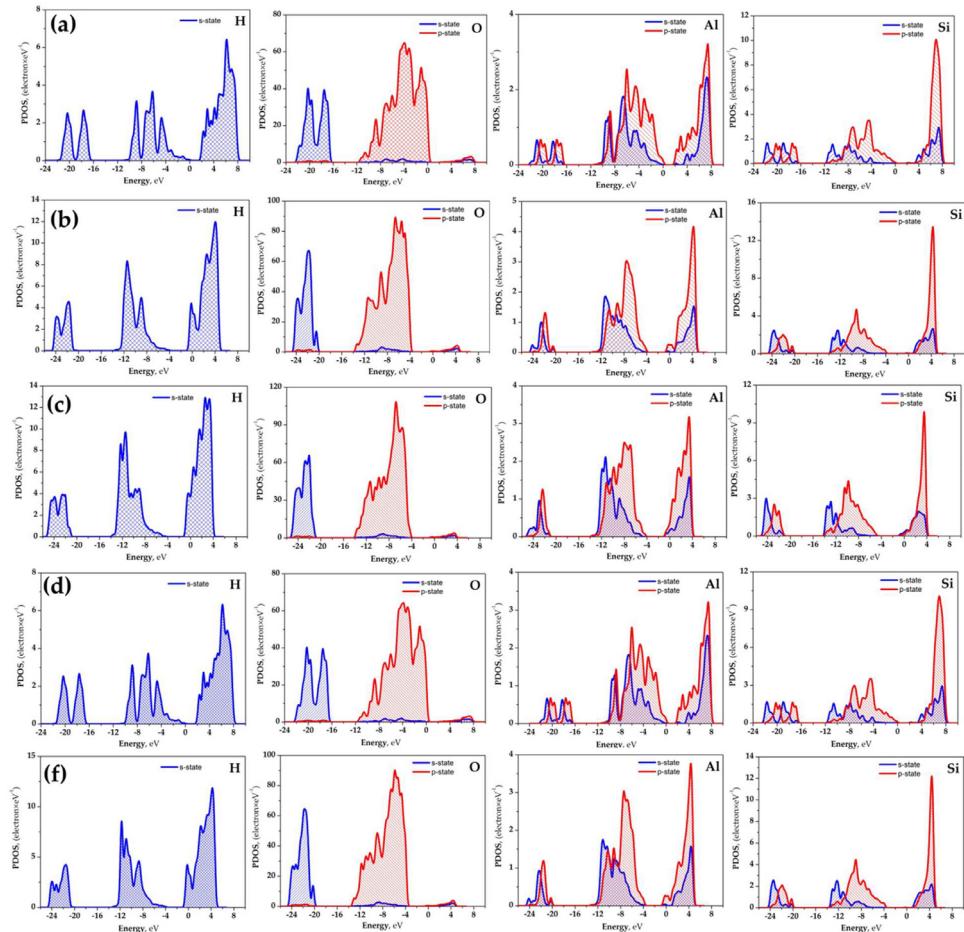
Presented in **Fig. 2** the partial density of electronic states (PDOS) characterizes the electronic structure of basal and edge mineral surfaces of kaolinite. PDOS determines the projection of the density of occupied electronic states onto the local orbital  $\mu$  of each atomic state and allows the characterisation of the state changes of the atoms of the mineral surface.

**Table 1** presents the charges of the terminal OH-groups obtained from Mulliken population analysis [1]. The population analysis was performed using the projection of plane wave states onto a localized basis using the technique of [2].

**Fig. 3** presents data on the change in the electrostatic potential of the mineral surface, as related to the energy required to remove an electron from the volume into the vacuum (work function). The average electrostatic potential in planes parallel to the mineral surface of kaolin-



**Fig. 1.** Models of kaolinite edge surfaces: (a) basal surface (001), (b) edge surface (010) with type I terminal-group structure; (c) edge surface (110) with type III terminal-group structure; (d) basal surface (001̄), (f) edge surface (010) with type II terminal-group structure.

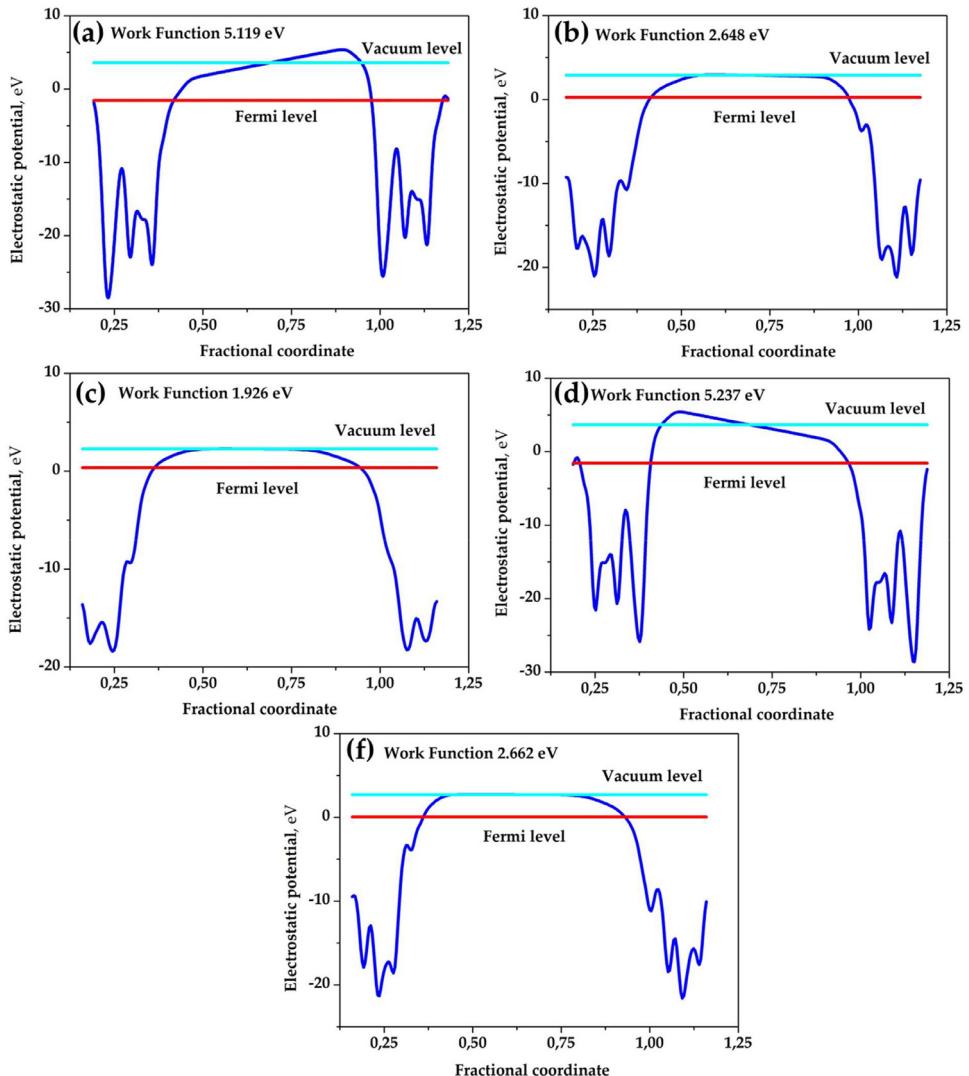


**Fig. 2.** PDOS of atoms of kaolinite edge surfaces: (a) basal surface (001), (b) edge surface (010) with type I terminal-group structure; (c) edge surface (110) with type III terminal-group structure; (d) basal surface (00̄1), (f) edge surface (010) with type II terminal-group structure.

ite is presented. The Fermi level is indicated on the work function diagram. The work function represents the minimum energy required to remove an electron from the crystal structure to a point just outside the mineral surface of kaolinite (the energy required to move an electron from the Fermi energy level into a vacuum). The work function depends on the crystal structure and surface orientation.

#### 4. Experimental Design, Materials and Methods

A supercell consisting of eight  $\text{Al}_{16}\text{Si}_{16}\text{O}_{40}(\text{OH})_{32}$  unit cells with 136 atoms and dimensional parameters of  $10.31 \times 8.94 \times 14.81 \text{ \AA}$  was used to construct models of kaolinite edge surfaces. The unit cell parameters and positions of OH groups were obtained from [3,4]. The edge surfaces of kaolinite were obtained by sectioning the three-dimensional structure along the following crystallographic planes: (001), (00̄1), (010) and (110). The position of the surfaces for mineral dissection was chosen to minimize broken bonds. Chemical sorption of water molecules to neutral total model charge was used to compensate for broken bonds.



**Fig. 3.** Averaged electrostatic potential and work function of kaolinite mineral surfaces: (a) basal surface (001), (b) edge surface (010) with type I terminal-group structure; (c) edge surface (110) with type III terminal-group structure; (d) basal surface (001̄), (f) edge surface (010) with type II terminal-group structure.

The first-principles package CASTEP [5] was used to obtain the optimized structure of kaolinite edge models. Calculations are performed in the generalized gradient approximation using PBE [6]. The cutoff energy of the basis set of plane waves is chosen to be 500 eV. The interaction between the valence electrons H(1s<sup>1</sup>), O(2s<sup>2</sup>2p<sup>4</sup>), Al(3s<sup>2</sup>3p<sup>1</sup>) and Si(3s<sup>2</sup>3p<sup>2</sup>) and the ionic backbone is described by the ultrasoft Vanderbilt pseudopotential [7]. The contribution of semi-core electrons was not used in the computational procedure. The geometry has been optimized with the following parameters: energy ( $10^{-5}$  eV/atom), maximum force ( $3 \times 10^{-2}$  eV/Å), maximum displacement ( $10^{-3}$  Å) and maximum stress ( $5 \times 10^{-2}$  GPa). The integration in the first Brillouin zone was performed based on a  $2 \times 3 \times 1$  Monkhorst-Pack mesh [8]. The k-point grid parameters have been determined on the basis of previous work [9,10].

**Table 1**

Mulliken charges of terminal OH-groups of kaolinite surfaces.

Surface	Terminal group	Atom	Mulliken charge		
(001)	<b>-OH</b>	O	-1.06	-1.05	-1.05
(010) with type I terminal-group	<b>H<sub>2</sub>O-Al-OH<sub>2</sub></b>	H	0.46	0.46	0.44
		Al	1.86		
		O	-0.96		
		H	0.31		
		H	0.29		
		O	-0.95		
		H	0.37		
		H	0.47		
		<b>Si-OH</b>	Si	2.24	
		O	-1.05		
		H	0.47		
(010) with type II terminal-group	<b>Al-OH<sub>2</sub></b>	Al	1.87		
		O	-0.92		
		H	0.48		
		H	0.47		
		<b>Si-OH</b>	Si	2.25	
		O	-1.09		
		H	0.53		
		<b>H<sub>2</sub>O-Al-OH<sub>2</sub></b>	Al	1.82	1.87
		O	-0.95	-0.95	
		H	0.46	0.48	
(110) with type III terminal-group	<b>Al-OH<sub>2</sub></b>	H	0.19	0.49	
		O	-0.96	-0.97	
		H	0.46	0.49	
		H	0.17	0.50	
		<b>Al-OH<sub>2</sub></b>	Al	1.84	
		O	-0.93		
		H	0.46		
		H	0.48		
		<b>Si-OH</b>	Si	2.21	2.16
		O	-1.02	-1.07	
		H	0.26	0.51	0.21

The contribution of van der Waals forces was taken into account in the DFT functional by introducing a dispersion correction of the form  $C_6R^{-6}$ , implemented in the Grimme scheme [11,12].

## Limitations

Not applicable.

## Ethics Statement

This article does not contain any studies with human, animals subjects or any data collected from social media platforms. The datasets used in the article are open to the public. For the usage of these datasets, proper citation rules should be maintained.

## Data Availability

Kaolinite edge surfaces (Original data) (Mendeley Data).

## CRediT Author Statement

**Anton Kasprzhitskii:** Conceptualization, Methodology, Validation, Supervision; **Alexander Kruglikov:** Data curation, Writing – original draft; **Yakov Ermolov:** Software, Visualization, Investigation, Writing – review & editing; **Anna Dolgova:** Investigation.

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## Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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