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Perspective

Mineral facets portray the fate of aquatic contaminants

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Mineral–water interfacial reactions determine the transformation, migration, and fate of contaminants in the environment. Depending on the thermodynamic and chemical conditions of the environment, mineral particles have different shapes, exposing several facets (Fig. 1a). For instance, natural hematite particles are enclosed by the {001} basal facet and edge {hkl} facets [1]. Pyrite crystals adopt a wide range of cubic, octahedral, and pyritohedral shapes with exposed {001}, {111}, and {210} facets, respectively [2]. In nature, a variety of crystal facets of minerals drive surface reactions, such as adsorption and desorption, redox transformation, precipitation, and dissolution. From the global and regional scales to the nanoscale and molecular scale, these reactions can lead to contaminant mobilization with destructive consequences for millions of people, such as groundwater arsenic contamination in Bangladesh [3]. Fundamentally, the environmental behavior of contaminants on natural minerals with multiple facets is the synthetic contribution of surface chemical reactions on specific single facets. Studying facet-specific interfacial reactions is crucial for deciphering complex and heterogeneous reactions across wide ranges of spatiotemporal scales in natural systems. This knowledge enables reliable extrapolation and prediction of the environmental fate of contaminants on natural mineral particles using state-of-the-art machine-learning algorithms.

With well-defined surface atomic structures of different mineral facets, such as three-, four-, and five-coordinated Fe sites on hematite {001}, {012}, and {110} facets (Fig. 1a), the interactions between contaminants and minerals can be clearly interpreted to understand the facet-dependent phenomenon. Regarding this, immense interest has increased in the past decades in facet engineering, particularly the exploration of the structure–property–performance relationship. One typical example is TiO_2, with different facets that are being actively used in environmental and materials science, and great efforts are being made to unravel the relationship between atomic structure and surface reactivity. In general, a mineral facet with high surface energy shows a high reactivity, which is closely associated with the form of surface undercoordinated atoms. On the anatase TiO_2 {101} facet, both five- and six-coordinated Ti atoms (Ti_{5C}, Ti_{6C}) exist, while 100% Ti_{5C} atoms are exposed on the {001} facet (Fig. 1a). The large amount of undercoordinated Ti_{5C} on the {001} facet enables a high surface energy, demonstrating superior reactivity in metal(loid) adsorption, organic pollutant degradation, and water splitting [4]. Thus, mineral facets with distinct surface atomic structures have specific reactivity, which controls the pathway, energy, and extent of surface chemical reactions.

At present, research on facet dependence has been limited to data from irregular mineral particles or only considers certain ideal facets. This limitation makes it demanding to relate experimental results to theoretical studies, and there are conflicting interpretations of the mechanisms involved. Although the cause of the reactivity difference on mineral facets has been intensively investigated, understanding of the facet-dependent phenomenon is far from complete. The importance of mineral facets in interfacial reactions cannot be overestimated: They portray the fate of contaminants and control the composition of our natural environment. In this work, a forward-looking perspective in mineral facet-dependent studies is proposed by recapitulating the main inferences drawn from the present work and directions for future investigations.

Identification and quantification of active sites at the mineral–water interface. Surface hydration is the very first step and is of paramount importance in solid–water interfacial reactions. When metal oxides are exposed to water, the surface O atoms become hydroxylated, and the hydroxide sites undergo protonation and deprotonation reactions, leading to pH-dependent surface charge and surface structural relaxation or reconstruction. Crystal truncation rod (CTR) analysis of the hematite {001} facet discloses that the hydrated surface differs significantly from the three possible terminations of the bulk hematite structure and is dominated by two hydroxyl terminations: The hydroxylated single-layer Fe termination of $(HO)_3$–Fe–H_3O_3–R and the hydroxylated oxygen termination of $(HO)_3$–Fe–Fe–R (Fig. 1b) [5]. An in-depth summary of the TiO_2–water interactions identifies that a key issue is whether or not water will dissociate on TiO_2 surfaces to form surface hydroxyl sites such as Ti_{5C}–OH and O_{2C}–H, depending on the surface atomic coordination and Ti–O–Ti bond energy (Fig. 1b) [4]. Adsorption modes of water on TiO_2 facets redefine active hydroxyl sites, and dissociative water adsorption at the Ti site on the {001} facet increases the energetic penalty for water exchange at the Ti site to accommodate contaminant molecules. These results underscore the influence of facet-dependent hydration on occupying active sites to impact the conjunction of contaminants.

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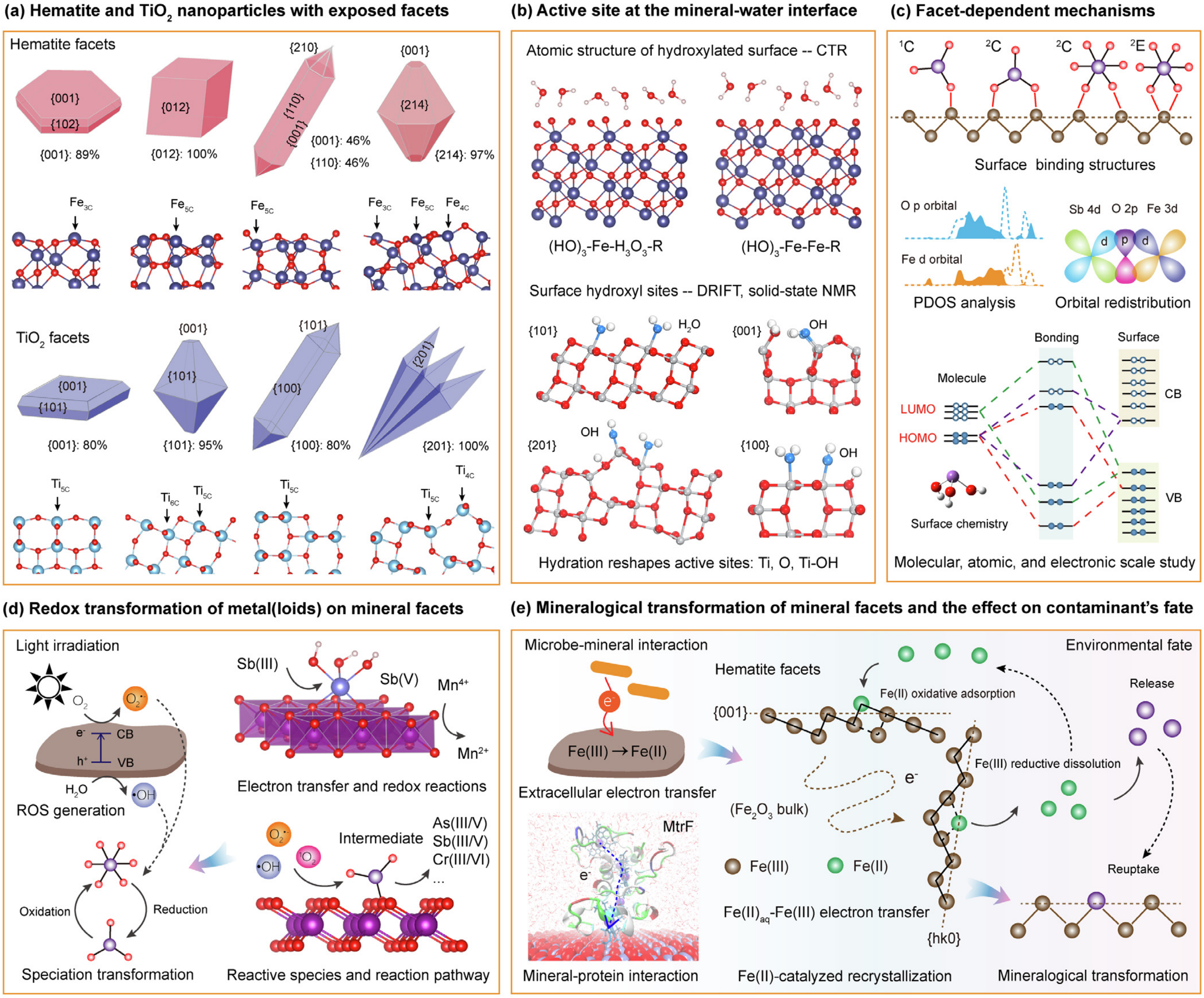

Fig. 1. Schematic illustration showing the environmental interfacial chemistry of contaminants on mineral facets. (a) Hematite and TiO_2 particles with dominant exposed facets and the atomic structures of different facets. (b) Mineral–water interfacial structure and surface active site characterization [5]. (c) The facet-dependent mechanism of interfacial reactions is an integrated study of binding structure, orbital redistribution, and electron transfer. (d) Reactive species production on mineral facets and their effect on the redox transformation of metal(loids). (e) Mineralogical transformation of hematite facets [1] and its impact on the fate of contaminants.

Identification and quantification of active sites at the mineral–water interface are the basis for understanding the mechanisms of facet-dependent interfacial reactions. On this subject, diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy, sum-frequency generation vibrational spectroscopy, Raman spectroscopy, solid-state nuclear magnetic resonance (NMR) spectroscopy, temperature-programmed desorption technique, atomic force microscopy, and synchrotron-based X-ray and neutron techniques are useful for detecting the nature of the active site and its acidity/strength on mineral surfaces [6–8]. On the other hand, density functional theory calculations are always coupled with these spectral studies to give atomic-level information.

Dynamically, the hydrated active sites are refreshed to accommodate the target molecules. The mechanistic study of solid–water interfacial reactions considering hydration effects is still challenging due to the difficulty in *in situ* detection of the interfacial dynamics of the water structure. *Ab initio* molecular dynamics (AIMD) simulations are insightful for inspecting the dynamic evolution of interfacial water on active sites at the atomic level. By integrating state-of-the-art characterization techniques and AIMD simulations, the structural evolution of the active sites at the mineral–water interface can be thoroughly revealed in future works, allowing novel, exciting possibilities for elucidating the mechanisms that govern the interfacial reactions of contaminants on mineral facets.

Mineral facet-dependent adsorption of contaminants and their mechanisms. Mineral facets with distinct atomic structures determine the adsorption structures of contaminants, playing a significant role in interfacial reactions to control the fate of contaminants. Extensive experimental and theoretical studies have elucidated the facet-dependent adsorption structures of As(III/V), Sb(III/V), Cr(VI), V(V), Pb(II), U(VI), methylmercury, and organic pollutants on hematite, pyrite, hydroxyapatite, TiO_2, MnO_2, and $BiVO_4$ facets. These reports show that in general, diverse corner-sharing monodentate mononuclear (^{1}C), corner-sharing bidentate binuclear (^{2}C), edge-sharing bidentate mononuclear (^{2}E), and edge/corner-sharing tridentate (^{3}T) binding configurations can be produced on the mineral facets (Fig. 1c). This heterogeneity of the adsorption modes of the contaminants is ascribed to coordination matching with the surface structure of the minerals.

Although the general understanding of the facet-dependent rationale is attributed to the surface atomic structure, the remaining experimental phenomena cannot be well explained. For example, an extended X-ray absorption fine structure (EXAFS) study of As(III/V) on three hematite facets presented undistinguishable As–Fe distances that are representative of the ^{2}C complex. However, the ^{1}C complex on the {0 0 1} facet is theoretically preferred, which is attributed to the stabilization of As(III/V) by hydrogen bonding [9]. These results underline three aspects that merit continuous exploration when researching the facet-dependent mechanisms of mineral–water interfacial reactions. First, the hydration effect on the coordination structure is critical. To bridge the experimental results with the predictions made considering the theoretical studies, simulation models should be constructed to mimic the actual solid–water interface. Second, EXAFS shell fitting provides an averaged result, but the rich structure may be shadowed by this characterization, which requires a comprehensive study of adsorption structures at diverse active sites on mineral facets in theoretical calculations to carefully interpret the spectroscopic results. Third, most EXAFS characterizations are for samples at reaction equilibrium, and information on the structural evolution during the reaction process is lacking. Using advanced quick EXAFS coupled with atomic-scale AIMD simulations, exploring the dynamical process of reactions at the mineral–water interface is a direction in future research.

To elucidate the facet-dependent mechanisms, the surface chemistry for contaminant adsorption should be investigated at the molecular, atomic, and electronic scales. When molecules bond onto the surface, electrons are generally transferred from bonding orbitals in one component to antibonding orbitals in the other, and a new bond is formed between the adsorbed molecule and the surface. Density of state analysis is the conventional method of obtaining electron localization information on orbitals, which is extensively conducted to interpret the orbital energy shift upon contaminant adsorption. Moreover, the projected density of state analysis clearly discloses the contribution of specific orbitals in the bonding to form stable surface complexes, such as the new Fe–O bond formed by electron sharing between O-2p and Fe-3d orbitals when Sb oxyanions adsorb on iron-containing minerals [10]. Basically, facet-dependent adsorption is based on the energy level of the Fe–O atom pairs, which can be estimated by the integrated crystal orbital Hamilton population. By applying this criterion, the facet-dependent bonding strength of contaminants can be determined. Thus, depicting the binding structure, electron transfer, and orbital redistribution is still an attractive topic for profoundly understanding the intrinsic mechanisms behind facet-dependent phenomena (Fig. 1c).

Mineral facet-dependent reactivity on the transformation of the contaminants. Minerals with semiconducting properties are sensitive to light absorption to generate electron (e^-)–hole (h^+) pairs and reactive oxygen species (ROS), such as hydroxyl radical (·OH), superoxide radical ($O_2{\cdot}^-$), and singlet oxygen ($^1O_2$), for the redox transformation of contaminants (Fig. 1d). Mineral facets with diverse atomic coordination environments have various orbital energy levels in the valence band (VB) and conduction band (CB), as well as the electronic states, influencing the interfacial electron transfer and the type and amount of ROS. For example, compared with the TiO_2 {1 0 1} facet, the stronger interaction of the {0 0 1} facet with molecular O_2 facilitates the transfer of photoexcited electrons to the adsorbed O_2 to produce $O_2{\cdot}^-$ and ultimately promotes As(III) photooxidation efficiency. Therefore, determining the oxidant/reductant species in redox reactions and examining the effects of surface electronic states on reactive species formation are promising approaches to elucidating the intrinsic nature of facet-dependent reactivity.

Direct electron transfer between adsorbed species and mineral surfaces is another pathway to mediate redox reactions. Manganese oxides (MnO_2) have attracted attention among the transition metal oxides because of their dissimilarity in redox properties, such as direct As(III)/Sb(III) oxidation on MnO_2 coupled with Mn^{4+} reduction to Mn^{2+} (Fig. 1d) [11]. MnO_2 facets vary in bonding strength, and electron transfer capacity can show a facet-dependent reactivity in the transformation of the contaminant. Therefore, elucidating the electronic structure of the frontier orbitals of the adsorbed intermediate species is promising for interpreting the facet-dependent mechanisms. Quantum calculations can help obtain electronic and atomic-level information. Theoretical results can make experiments more tractable by helping in their interpretation and narrowing the number of possible reaction pathways that likely exist in dynamic environments.

Nevertheless, myriads of reports have disclosed the effect of facets on redox reactions, such as As(III) and Sb(III) oxidation and Cr(VI) and U(VI) reduction. However, the reactivity of mineral facets remains under debate. More investigation is still needed regarding the facet-dependent mechanism in terms of atomic construction and electronic states. In future work, it is crucial to examine several critical features to understand the facet-dependent reactivity: (1) The mechanisms of interfacial electron transfer and the chemical nature of reactive species, (2) the dynamics of redox reactions of contaminants with reactive species on the facets, (3) the detection of intermediate species and the effect of facets on the binding structure of the intermediate, (4) the investigation of electronic structure of intermediate species after facet-dependent adsorption, and (5) the estimation of pathway and thermodynamics in redox reaction steps.

Mineralogical transformation of mineral facets and their effect on the fate of the contaminants. Minerals undergo dissolution and growth when they contact aqueous solutions that are not in equilibrium as the system tries to reach a new equilibrium. Environmental conditions (such as temperature, humidity, fluid composition, light irradiation, and microorganisms) can influence the equilibrium state of minerals and prompt mineralogical transformation. This process includes electron transfer and atomic exchange, which are particularly dependent on mineral facets with distinct surface atomic and electronic structures. Facet-dependent phenomena commonly exist in several processes, such as the recrystallization of hematite catalyzed by Fe (II), the oxidative dissolution of CdS by light irradiation, the moisture-controlled oxidation of pyrite, and the dissolution of α-quartz crystals in silica-undersaturated water [1,12,13]. These results underscore that mineralogical transformation is reconceptualized in terms of coupled redox dissolution and oriented growth driven by facet-specific adsorption and electron transfer, strengthening the important influence of facets on transformation outcomes.

Microorganisms drive the biogeochemical cycles of elements and mineralogical transformation. Facet-preferential microbial Fe(III) reduction on the hematite {0 0 1} facet, rather than the {1 0 0} facet, has been studied [14]. In microbial-driven Fe oxidation or reduction, electrons are transferred by cell surface-localized *c*-type cytochrome proteins, which can catalyze the direct extracellular electron transfer through a multistep hopping mechanism along the heme chain [15]. Therefore, the crucial question is how mineral facets influence the configuration of the cytochrome protein to impact the electron transfer pathway (Fig. 1e). In this regard, a study of mineral–protein interfacial reactions at the molecular and atomic levels by using spectroscopic techniques and MD simulations is promising. The facet-dependent effects on other extracellular electron transfer pathways, such as nanowires and electron shuttles, are also compelling research areas that need to be extended in the future.

Facet-dependent mineralogical transformation can be generalized to other minerals with redox-active metals, such as environmentally wide-distributed iron and manganese oxides and sulfides. Currently, research on how different facets of minerals affect the mineralogical transformation and their impact on the fate of contaminants is still in its nascent stages. A number of unresolved issues warrant further investigation (Fig. 1e). First, the effect of facets on mineral transformation has not been established completely. The redox reactions and elemental cycling need further exploration for a set of facets of different minerals to determine the general law of facet-dependent mineralogical transformation. Second, the effect of mineral facets on microbially induced mineralogical transformation merits further research, in particular mineral–microbe interaction at the molecular level. Third, the compounding effects of environmental factors on mineralogical transformation have not yet been considered, which should be addressed to highlight the actual implications of the facet-dependent phenomena. Fourth, the effects of mineralogical transformation on the fate of contaminants require much research using a combined approach of *in situ* spectroscopic characterizations and theoretical calculations. Fifth, most natural mineral particles are composed of multiple crystal facets, and the synergistic or competitive effect of the coexisting facets on the interfacial electron transfer, mineralogical transformation, and mobilization of contaminants requires further exploitation.

In summary, mineral facets play a dominant role in determining the mineral–water interfacial reactions and controlling the geochemical cycling of elements. Essentially, the different atomic structures and active site distributions on the facets should influence all types of reactions at the mineral–water interface. By exploring the generality of the facet-dependent phenomenon for various mineral facets, a comprehensive understanding of the environmental fate of contaminants can be established. Moreover, the examination of facet-dependent impacts and the underlying mechanisms undoubtedly improves the scope of environmental interfacial chemistry and progressively establishes a key foundation for further interdisciplinary investigations in the fields of environment, energy, and materials.

Conflict of interest

The authors declare that they have no conflict of interest.

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