

Editorial

First-Principles Calculations of Minerals and Related Materials

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As stated in their announcements and accompanying information, Special Issues published in scientific journals are usually aimed at compiling recent progress on highly specialized topics. The articles put together in Special Issues tend to be unrelated to each other when they involve more general topics. An important achievement in such cases, although often unintended, relates to the information contained in the published papers in relation to the current state of the subject area. For instance, one may take a careful look at the tools, methodologies or approaches that are commonly employed by researchers working in the field. This is the case for the present Special Issue, “First-Principles Calculations of Minerals and Related Materials”, which provides a snapshot of the quantum-mechanical computational methods that are currently being employed for research in mineralogy and geochemistry.

At first sight, the present Issue covers a broad range of topics, including high-pressure lattice dynamics calculations, adsorption of rare earth elements in clay minerals and crystal structure prediction of rare minerals. However, a closer examination allows one to classify all the published manuscripts in two broad categories: (i) density field theory (DFT) simulations to investigate the fundamental properties of crystals [1–5] and (ii) study of adsorption and chemical reactivity in mineral surfaces by molecular dynamics (MDs) calculations based on DFT [6–10].

With regard to the first category, the work by Cheng and co-authors dealing with the effect of carbon impurities at sulfur/iron vacancies on the electronic and optical properties of pyrite associated with coal [2] provides a helpful example about the usefulness and popularity of DFT to investigate the fundamental properties of minerals and related compounds. Indeed, *ab initio* calculations are widely used in different research areas, such as solid-state physics, materials science or nanoscience, to deepen the knowledge on the studied ‘pristine’ crystalline phases, as well as to investigate low-dimensional systems, alloys, doped materials or heterostructures. In addition to being a well-known mineral, pyrite (fool’s gold) is being actively investigated due to its great potential as a cheap photovoltaic material.

It is interesting to note that up to four of the five published papers on DFT calculations published in this Issue deal with high-pressure conditions. This shows the effectiveness, not far from supremacy, of DFT calculations to investigate the compression behavior of solids. Today, researchers routinely use DFT to obtain pressure–volume equations of state, compressibility, elasticity or compliance properties, phonon and band-gap pressure coefficients, phase-transition pressures and enthalpies, etc. In the case of the present work, the compounds investigated under pressure include phyllosilicate minerals such as pyrophyllite [1], layered transition metal dichalcogenides (TMDCs) such as rheniite (ReS₂) [3], or rare minerals such as zaccariniite (RhNiAs) [5].

With regard to the interesting topic of high-pressure research, it is worth mentioning the essay paper by Manjón et al. [4] included in this Issue. This manuscript highlights the relevance of employing combined methodologies that include experiment (high-pressure Raman spectroscopy) and theory (DFT) in order to properly understand the lattice-dynamical properties of crystalline materials, not only upon compression but also at



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room pressure conditions. This joint experimental and theoretical approach was recently employed by Manjón and collaborators to investigate numerous different compounds, such as sesquioxides [11,12], ordered-vacancy compounds [13,14], topological insulators [15–17] or in relation to metavalent bonding [18]. The paper by Manjón et al. [4] also serves as a prelude to Ref. [5] in this Issue. In that work, using the mineral zaccariniite as a working example, the usefulness of the methodologies proposed by Manjón and colleagues is further explored in order to structurally characterize rare minerals.

On the other hand, MD simulations have become increasingly popular over the last few decades in order to gain information about atomic and complex adsorption in solid surfaces and also to understand chemical reaction mechanisms on surfaces. In this Issue, the types of problems that have been tackled by different groups include the adsorption of As complexes on cobalt ferrite (Fe_2CoO_4) surfaces [8], the recovery of rare elements adsorbed on the argillaceous mineral kaolinite [10] or the role of Mg impurities in the water adsorption in calcium silicate phases that are predominant in ordinary Portland cement [6]. These studies are useful to highlight the importance of DFT and MD studies in relation to cementitious phases, the recovery of critical elements by using clay minerals or the management of mobile inorganic contaminants. In particular, the study on calcium silicate phases (Ref. [6]) adds to the previous work by Wang et al. [19], published in the Special Issue “Molecular Simulation of Mineral-Solution Interfaces” in this journal, in relation to water adsorption on the surfaces of calcium silicates.

In addition to these highly interesting topics, we would like to remark the importance of first-principles calculations for research related to carbon capture. A useful example of this is provided by Mutisya and Kalinishev [9] in this Issue, who explore the reactivity of supercritical CO_2 with different surfaces of portlandite, i.e., one of the main phases resulting from the hydration reactions of Portland cement. These authors also study the role of water in the CO_2 –portlandite interaction. Similar studies in the future may be expected to shed light on the optimal conditions for carbon capture by different material systems. For this purpose, it might be useful to take into account other phenomena, such as, for example, the resistance of solid phases to weathering agents or the role played on carbon capture mechanisms by the liquid state.

The bright future of MD simulation theory is clearly exemplified by the perspective article by Rimola and colleagues [7], dealing with computational chemistry methods to investigate the physico-chemical properties of solid-state interstellar and interplanetary grains. While surface modelling is widely employed in many different research areas, such as catalysis and surface science, its application for astrochemical studies is still in its infancy. These authors discuss the state-of-the-art methodologies and strategies (construction of cluster models, algorithms, use of machine learning methodologies, etc.) to perform computational chemistry modelling of grains, like water ice or olivine, including the important case of amorphous and ‘dirty’ phases. The results obtained from quantum-mechanical simulations of these non-terrestrial materials may be particularly relevant in the near future in order to analyze the observational data provided by unique instruments, like the James Webb space telescope (JWST), operating in the infrared spectral range. Novel research on these highly interesting topics may be expected to generate great excitement and amusement in the astrochemistry and mineralogy realms soon, giving rise to highly compelling, if not unexpected, results.

In summary, the articles published in this Special Issue are representative of the way in which researchers employ first-principles calculations for their current research in mineralogy and related areas. As shown in the different works included in this compilation, DFT calculations and MD simulations are being actively used by mineralogists to solve an endless number of research problems. These computational techniques will be intensively used in the future to tackle new scientific challenges dealing with important topics, like climate change mitigation, astrochemistry or high-pressure research.

Conflicts of Interest: The author declares no conflict of interest.

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