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Special Issue
Solid Solutions: From Theory to Experiment

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Letter to the Editor

Solid solutions: from theory to experiment

The idea to this special issue was born at the Goldschmidt Conference 2004 in Copenhagen. We found that the papers presented in the special session on solid solutions clustered within certain mineral groups. In each such cluster of topics, theoretical and experimental studies complemented each other in a remarkable way. Thus, the underlying scheme of this special issue is not just solid solutions in general, but how the combination of computational sciences and laboratory experiments can lead to a comprehensive understanding of thermodynamic, structural and other physico-chemical properties of solid solutions. In order to achieve this goal in this issue, we have invited other experts in the field to complement the collection of papers.

Already in prehistoric times, a specific type of “solid solutions”, that is alloys, have been used for all kinds of purposes. Back then, it was more of a trial and error approach to find materials that were suitable for making tools with specific physical properties. In the Earth Sciences, solid solutions have attracted attention since the early 1900s, that is, once it became possible to study the structure and composition of minerals. Rocks consist of minerals and most of them are substitutional solid solutions. The amount of substitution possible is in most cases a sensitive function of the temperature and pressure of formation. Therefore, a thorough knowledge of the thermodynamics of solid solutions is the basis for using solid solutions or mixed crystals, as they are sometimes termed, as geothermometers and geobarometers. In addition, an understanding of ordering processes gives further insight into formation processes of rocks and minerals and into transformation processes during metamorphic events. In a similar way, the conditions of formation (pressure, temperature, cooling rate, etc.) determine the partitioning of the substituting ions between a solid solution and the corresponding parent phase.

Advances in experimental methods employed to study the structure and chemistry of solid solutions, especially the resolution at which structural and chemical changes can be studied, enable us to gain a deeper insight in these ordering processes. What used to be homogeneous solid solutions fifteen years ago may now reveal, e.g., oscillatory zoning at the nanometer scale. These observations are complemented by a growing number of computer models that are based on atomistic and sometimes quantum mechanical principles. These computations are crucial where thermodynamic data are impossible to be obtained from experiments, e.g., because equilibration temperatures are low and, therefore, equilibration times too long to be studied in the laboratory. In addition, computer simulations can teach us about ordering processes at a scale that is currently not available by any experimental technique.

Physico-chemical and electronic properties of minerals are often highly dependent on the composition of solid solutions. These properties are typically not a linear function of the mole fractions of the endmembers. Therefore, the science of solid solutions is not only a growing field within the Earth sciences but also within materials science research. Admixtures of small amounts of one substituent into an otherwise homogeneous substrate can significantly change the electronic structure and elastic properties of this substrate. In fact, a significant number of computational methods that we apply now in geological sciences such as cluster variation methods are inspired by the alloy and metallurgical science community.

Solid solutions are geochemically and environmentally important because the interaction of dissolved toxic metals with minerals frequently results in the precipitation of metal-bearing solid solutions on the mineral surfaces or in rock or sediment pores. These

substitutions can be cationic or anionic. As a result, metals can be removed from natural waters and the thermodynamic properties of these solid solutions have a vital influence on the transport and fate of toxic metals in the environment. Therefore, a thorough knowledge of the thermodynamics of materials containing mixed crystals allows us to optimize passive and permeable remediation barriers and other environmental technologies.

Solid solution effects are important in quantifying element budgets and flows among different Earth reservoirs, i.e., in considering the biogeochemical cycles of the elements. Since thermodynamic properties are not a linear function of the composition, related properties such as the solubility product are not linearly dependent of the composition either. This phenomenon significantly influences the formation and partitioning in biomineralization processes and is a key parameter for gathering information about past climates and ocean productivity from marine geochemical records. This can be studied using authigenic sedimentary minerals such as sulfates and carbonates.

However, in order to familiarize the reader with some modern concepts of treating processes in solid solutions, this issue starts with five conceptual papers. Purton et al. review some state-of-the-art computer methods currently applied to study thermodynamic and ordering phenomena in solid solutions. Kulik describes a method to model equilibrium speciation, activities, and element partitioning in a heterogeneous system such as the aqueous-solid solution system to estimate interaction parameters of non-ideal mixing models from known bulk compositions of coexisting aqueous and solid-solution phases, and to determine stoichiometries and standard chemical potentials of trace solid-solution end-members. Goodwin et al., Burton and van de Walle, and l'Heureux and Katsov complement this introductory series of conceptual articles using applications to specific solid solutions. Goodwin et al. use the concept of rigid unit modes of SiO_4 tetrahedra to study cation substitution and strain screening in silicate framework structures. The contribution by Burton and van de Walle describes how the incorporation of the entropy of vibration into the Hamiltonian (in most computational studies, only the configurational entropy is considered) can dramatically improve the temperature dependence of phase diagrams. Finally, l'Heureux and Katsev introduce the concept of macroscopic and cellular automata models and apply it to oscillatory zoning in a $(\text{Ba},\text{Sr})\text{SO}_4$ solid solution as it may occur from the core to the rim of sulfate crystals.

Each of the minerals classes in the special issue is introduced by one or more theoretical studies. This concept is an important part of this special issue to make it easier for the reader to see the relationship between theoretical approaches and experimental studies. It also shows the status quo of both theory and experiment, where they complement each other and where the current limitations of both approaches are.

The next topical cluster of this special issue deals with sulfates, sulfides, and carbonates. An example for a study combining molecular simulations, macroscopic crystal growth experiments, and nanoscopic *in situ* AFM observations on an anionic solid solution is presented by Becker et al. The simulations allow determining the mixing properties of the hashemite solid solution and establishing the thermodynamics of the $(\text{BaSO}_4\text{-BaCrO}_4)\text{-H}_2\text{O}$ system. The crystal growth experiments are presented on the basis of this thermodynamic framework. The system is important from an environmental point of view, since surface precipitation of hashemite on barite could be a potential way to remove Cr(V) from aqueous environments. Another example for an anionic solid solution is the experimental study by Fernández-González et al., which is the $\text{Ca}(\text{SO}_4,\text{SeO}_4)\cdot 2\text{H}_2\text{O}$ solid solution within the gypsum framework structure. From their results, a thermodynamic model for the $\text{Ca}(\text{SeO}_4,\text{SO}_4)\cdot 2\text{H}_2\text{O}\text{-H}_2\text{O}$ solid solution-aqueous solution system was developed. Staying with sulfates but with cationic substitution, Sánchez-Pastor et al. deal with the relationship between habit and compositional changes in crystals of the $\text{Ba}_x\text{Sr}_{1-x}\text{SO}_4$ solid solution. The results presented in this paper help to develop morphological criteria relating morphology and composition of $\text{Ba}_x\text{Sr}_{1-x}\text{SO}_4$ crystals occurring in natural environments as a result of inorganic crystallization and biomineralization processes.

The transition from sulfate-containing solid solutions to its reduced counterpart, sulfides, requires a somewhat different treatment. The ionic properties of the sulfates become more covalent in sulfides and insulating properties become more (semi-)conducting. Therefore, the theoretical study of iron sulfides and arsenides by Reich and Becker requires a quantum mechanical treatment. Their findings are the basis for understanding metal incorporation as a function of arsenic content. The experimental study by Hem extends the system to cationic and anionic substitution and includes Co and Ni replacement for Fe.

The next group of solid solution compositions treated in this special issue are carbonates. As in the previous mineral classes, this theme block is introduced

by a theoretical study by Vinograd et al., who develop a set of interatomic potential parameters to derive the thermodynamics of carbonate solid solutions with different cations. This theoretical study is complemented by the experimental approaches by Fernández-Díaz et al. and Astilleros et al. Fernández-Díaz et al. focus on morphology changes of calcite crystals due to the incorporation of other divalent cations and relate their findings to morphology changes that may be interpreted as being caused by biological processes. Astilleros et al. use atomic force microscopy to study the influence of other divalent cations on growth mechanisms and rates of CaCO_3 polymorphs.

More complex structures are treated in the silicate theme block which focuses on garnets. Lavrentiev et al. use a combination of Monte-Carlo and lattice-dynamics calculations to derive the thermodynamics of pyrope-almandine and pyrope-grossular solid solutions as a function of pressure and temperature, which can be an important database for evaluating processes in the Earth's mantle. Oberti et al. apply a number of electron microbeam and synchrotron-based techniques to determine the bonding environment of cations in garnets. This approach can help to explain both the strong and asymmetric non-ideality of the solid solution between pyrope (almandine) and grossular, as well as the differences in the ability to incorporate some trace elements (such as REE and actinides), which are commonly used as process-specific indicators. Finally, Boffa-Ballaran and Woodland use powder IR absorption spectroscopy to characterize cation substitutions in three garnet solid solutions: grossular-andradite, skiagite-andradite and skiagite-almandine. More complex silicates are treated by Neuhoff and Ruhl by evaluating the different substitution mechanisms in zeolites. Some of their findings allow to perform thermobarometric calculations in very low-grade metamorphic and diagenetic environments. The composition dependence of glass formation is examined by Richet et al. in a variety of silicate systems that include alkali and alkaline earth alumino-, titano-, ferro-, and ferrisilicates. They describe the correlation between the extent of glass formation,

possible crystallization from the melt of numerous compounds, and moderate liquidus temperatures.

Mirão and Figueiredo determine the pattern of minor element incorporation in columbites ($\text{A}^{2+}\text{B}_2^{5+}\text{O}_6$) from granitic pegmatites using synchrotron radiation X-ray fluorescence (SRXRF) data; major elements (Fe, Mn, Nb, Ta) were analyzed using electron microprobe analysis (EPMA). In addition to their economic importance as niobium and tantalum ores, columbites display physical properties that make them adequate prototypes for oxide materials with relevant technological applications.

Even though this special issue can only cover a small selection of solid solutions and a limited number of methods to describe them, we hope to have shown, how far experimental and theoretical techniques have come along to complement each other to obtain a detailed description of thermodynamic, structural, and electronic properties of solid solutions. Equally important, this special issue will also show where the shortcomings of present and challenges for future research are. For example, theoreticians will need more thermodynamic data from experimentalists to verify their computational data, and more of the theoretical work will have to be based on accurate quantum mechanical calculations. Experimentalists studying solid solutions have made great progress in understanding ordering processes at smaller and smaller scales and this journey has not reached its end.

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