



Full length Article

# Crystallization behavior of solid solutions from aqueous solutions: An environmental perspective

Manuel Prieto <sup>a,\*</sup>, Frank Heberling <sup>b</sup>, Rosa M. Rodríguez-Galán <sup>a,b</sup>,  
Felix Brandt <sup>c</sup>

<sup>a</sup> Department of Geology, University of Oviedo, C/ Arias de Velasco, s/n, 33005 Oviedo, Spain

<sup>b</sup> Institute for Nuclear Waste Disposal, Karlsruhe Institute of Technology, 76021 Karlsruhe, Germany

<sup>c</sup> Institute of Energy and Climate Research (IEK-6) – Nuclear Waste Management and Reactor Safety, Research Centre Jülich GmbH, 52425 Jülich, Germany

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## Abstract

Aqueous–solid solution (AQ-SS) processes have garnered increasing attention from geochemists and environmental engineers because they play major roles in the fate and transport of elements in Earth surface environments. The reasons for this interest include: (i) the primary crystallization of minerals from multicomponent aqueous solutions leads to the formation of solid solutions in which different ions are substituted for one another in equivalent structural positions; (ii) the interaction between pre-existing minerals and water frequently yields surface precipitation and dissolution–recrystallization processes in which such substituting ions redistribute to adapt to new physicochemical conditions; (iii) the concentrations of specific minor elements in biogenic and abiogenic minerals have been shown to correlate with various parameters characterizing the growth environment (temperature, pH, nutrient levels, salinity, etc.) and the corresponding compositional signatures can be powerful tools in reconstructing the past from the sedimentary record; (iv) the aqueous concentration of heavy metals and other harmful ions can be significantly reduced by their incorporation into the structure of suitable host minerals and as such a ‘reduction of solubility’ can be exploited as a remediation strategy or used to design engineered barriers for the retention of metals, radionuclides, and other industrially generated inorganic wastes. In this review, the thermodynamics driving of AQ-SS processes is presented using examples of environmentally-relevant systems. The reaction pathways in AQ-SS processes depend not only on thermodynamic factors but also on kinetic and mechanistic effects, which operate at different scales in space and time. Examples of such effects include non-equilibrium ion partitioning, surface passivation, and compositional (sectorial, concentric, oscillatory) zoning. Finally, we discuss the contribution of both state-of-the-art characterization techniques and molecular simulation methods for the development of predictive models.

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## 1. Introduction

When two or more dissolved ions have similar size and chemical affinity, co-precipitation to form

solid-solution crystals is likely to occur. Indeed, solid solutions are ubiquitous in both natural and industrial scenarios. In Earth surface aqueous environments, the primary crystallization of minerals often leads to the formation of solid solutions, *i.e.* non-stoichiometric solids in which two or more ions substitute each other in equivalent structural positions. Moreover, foreign ions can be taken up from water during mineral–water interactions resulting in solid phases with substitutional impurities in major,

\* Corresponding author. Department of Geology, University of Oviedo, C/ Arias de Velasco, s/n, 33005 Oviedo, Spain. Tel.: +34 985103088; fax: +34 985103088.

E-mail address: [mprieto@geol.uniovi.es](mailto:mprieto@geol.uniovi.es) (M. Prieto).

minor, or trace amounts. Aqueous–solid solution (AQ-SS) processes have gained increased attention over the last few decades, not only because of the role of solid solutions as sequestering phases for harmful ions [1,2] but also because of their relevance in reconstructing past conditions in Earth surface environments [3–5]. Here, we address the factors that regulate the AQ-SS processes and discuss their environmental implications, which include:

- (I) Immobilization of pollutants. Solid-solution formation can control the mobility of harmful ions in the environment and is frequently exploited in the design of barriers engineered for the retention of metals, radionuclides and other industrially generated pollutants. The driving factor arises from the fact that the equilibrium aqueous concentration of a minor element  $C$  incorporated in a solid solution  $(B,C)A$  can be significantly lower than its concentration at equilibrium with the pure  $CA$  solid [6]. The role of solid solutions as sequestering phases is widely recognized in environmental studies [1,2,7], but the cocrystallization effect is often disregarded in water–rock interaction geochemistry, which focuses primarily on surface adsorption [8].
- (II) Record of past environmental conditions. AQ-SS systems can provide noteworthy information about past environmental changes and global element cycles. For instance, the concentrations of certain minor elements (Sr, Ba, Mg, etc.) in calcium carbonate minerals precipitated by marine organisms are typically used as signatures of the growth conditions, which among other factors include temperature, carbonate concentration, nutrient levels, and salinity [9]. Such an application requires a rigorous knowledge of the thermodynamic, kinetic and crystallographic mechanisms that come into play, as well as an evaluation of the role of the so-called *vital effect*, *i.e.* the biological factors affecting trace element partitioning in such systems [10,11].

While the environmental implications are underlying throughout the whole article, the text is essentially arranged on a physical-chemical basis, starting from the equilibrium thermodynamics of simple AQ-SS systems to finish with complex systems (multi-site and heterovalent substitutions, non-isostructural end-members, etc.) and non-equilibrium effects. Nucleation and growth of solid solutions is a thermodynamically driven process regulated by both the solubility of the pure end-member components and the free energy change needed to form a

substitutional solid solution from a compositionally equivalent mechanical mixture of the pure end-members [12]. However, thermodynamics is insufficient to account for the actual crystallization behavior in AQ-SS systems. Kinetic and mechanistic factors, which operate at different scales in space and time, usually play a major role in the nucleation and growth of solid solutions and determine the crystal composition. The available models [13–15] developed to predict AQ-SS processes are to some extent unsatisfactory, but all of them have the virtue of identifying the main concerns and the work that has to be done to progress in this field.

Because of its fundamental relevance and environmental implications, the development of compositional zoning [16] is discussed in a separate section. During growth, the substituting ions are not incorporated into the solid phase in the same ratio as in the aqueous phase. Therefore, both aqueous and solid compositions tend to change, and the crystals can develop concentric, compositional zoning. Concentric zoning patterns record the growth history in the AQ-SS system and are inherently non-equilibrium configurations. Even in the hypothetical case in which ‘partial equilibrium’ [17] is maintained between each growth layer and the solution composition at the time of its formation, reaching true-equilibrium would require ongoing dissolution–recrystallization to form a crystal of homogeneous composition at equilibrium with the remaining aqueous solution. Depending on the crystallization scenario a variety of concentric patterns can develop, of which the most striking are oscillatory [18]. The occurrence of oscillatory zoning (OZ) has drawn the attention of numerous scientists from different fields that have provided a wealth of hypotheses to explain their causes [19,20]. Typically, the hypothesis is implemented in a computer model that is considered functional only if it produces oscillatory solutions. In practice, despite the success in obtaining OZ patterns, most models disregard the physical-chemical workings of the system [21] and are qualitative by nature. Solid solution crystals frequently exhibit compositional sector zoning as well, which means that the relative incorporation of the substituting ions is different on different crystallographic faces of the same crystal. The reason for this becomes clear when we consider that an atomic site in the bulk structure may have different configurations when exposed on different faces of the crystal surface [22]. The surface-entrapment model proposed by Watson [15] is based on the idea that during crystal growth foreign ions adsorbed on surface sites can be ‘buried’ into the bulk crystal in a proportion that depends on the growth rate. The model provides a qualitative explanation for both concentric and sector zoning,

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