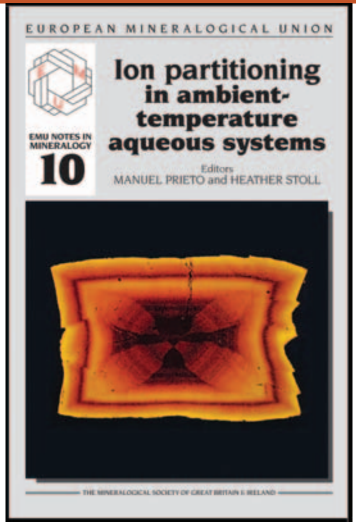
ION PARTITIONING IN AMBIENT-TEMPERATURE AQUEOUS SYSTEMS[1]



Water–rock interactions are at the heart of many of the processes that make the Earth (so far) a habitable planet[2]. Understanding and quantifying these processes help us to study, control and potentially remediate some of the anthropogenic interferences and disturbances affecting the delicate balance that makes life on Earth so unique. Natural and man-made systems are seldom simple, and this also applies to the interactions between complex solid solutions and multicomponent aqueous systems. In spite of this complexity we have to seek solutions because, as the late Werner Stumm used to say, "Everything that is interesting in Life happens at interfaces."

In this context, I responded with trepidation to the challenge posed by *Elements* of reviewing this book, which touches on a subject that has entertained me for many years. The same theme was treated in a book I co-authored, in 2007, with some of the contributors to this one[3]. Reading the book, the questions I asked myself were: How much has the field advanced in the last four years? Have we filled in some of the knowledge gaps we identified earlier?

The emphasis of the present book is broader, in the sense that the work edited by Manuel Prieto and Heather Stoll is not exclusively concerned with trace elements and radionuclides in aqueous solution–solid solution systems. The strength of the book resides in its overview of ion partitioning research in low-temperature systems.

Carbonates are the most often referred-to system in the 12 chapters of the book. In chapter 1, Prieto uses the Cd(II)–Ca(II) carbonate system to illustrate the effect of ionic strength and aqueous composition on measured distribution coefficients and the Zn(II)–Ca(II) carbonate system to point out non-ideality effects on solid solution behaviour. In chapter 2, Putnis uses the Cd–Ca carbonate system to illustrate the departure from equilibrium, and the divalent carbonate system to explain the effects of crystal anisotropy and surface structure on the kinetics of ion partitioning and the consequences for oscillatory zoning. The comprehensive chapter 3, by Kulik, touches on the carbonate system only in the discussion on regular interaction parameters. Divalent carbonates are central in chapter 4, in which Böttzer and Diechtel describe metal-ion partitioning during low-temperature precipitation and dissolution of anhydrous carbonates and sulphates. The equilibrium partitioning of divalent cations in calcite, aragonite, rhodochrosite and siderite is used to introduce various empirical and modelling relationships. Magnesian calcites are discussed with regards to the effect of congruent and incongruent dissolution on metal-ion partitioning. The formation of diagenetic carbonate from evaporitic sulphate is mentioned in some of the sections in chapter 5, by Putnis and Fernández-Diaz. In chapter 6, by Monnin and Herau, a full section is devoted to the carbonate system in the marine environment, in which the authors discuss some of the fundamental and experimental challenges regarding the carbonate system in seawater. In chapter 7, Fairchild and Hartland portray the influence of changing composition, colloid content and temperature of the contacting waters on the trace element content of speleothems. Godselitas and Astilleros in chapter 8 present the interaction of carbonates with heavy metals and actinides. The carbon cycle is introduced in chapter 9, by Oelkers and Gislason, who postulate that divalent carbonate formation is the main driving force for the long-term sequestration of injected CO_2. The interaction of trivalent actinides with calcite is discussed by Bosbach in chapter 10. In chapter 11, Cohen and Gaetani investigate the partitioning of divalent cations (Mg, Sr, Ba) in coral and abiogenic aragonite. They consider factors that influence the growth of biotic and abiotic aragonites, with implications for the use of coral skeletons as paleothermometers.

In chapter 12, Stoll uses the Cd–Ca carbonate system to illustrate ion partitioning in foraminifera and coccoliths, the largest producers of carbonate in the oceans. The Ca/Ba ratio in coccoliths is used to explain the influence of seawater concentrations on the partitioning of these elements in biotic carbonates. The Mg/Ca ratio in foraminiferal calcite records temperature variations in the ocean, and borate to carbonate partitioning in the same species gives some insights about the bicarbonate concentration and consequently the pH. Underlying all these discussions is a fundamental knowledge of the thermodynamic and kinetic controls of ion partitioning in carbonates, a theme that percolates through all the chapters in the book.

The second most studied systems in the book are the sulphates. Ca(II) and Ba(II) sulphates are ubiquitous in nature, and the interaction of Sr(II) and Ra(II) with them are at the heart of the development of aqueous solution–solid solution thermodynamics. This is largely reflected in the book, where these systems are described in chapters 1, 4, 6, 8 and 10.

In this book, the reader will find a large amount of up-to-date information regarding ion partitioning and its interaction with the carbon and sulphur cycles. The fundamentals are thoroughly developed in chapter 1, and some interesting applications are found in many of the chapters, particularly applications that interface between abiotic and biotic systems. While the broad scope of the book is one of its strengths, it also constitutes its weakness. Chapter 3 on geochemical modelling is too broad and too ambitious; many systems are modelled, but not a single experimental datum is used to contrast the plausibility of the models. Chapter 8 is also too broad, attempts to cover too many systems, and avoids the in-depth analysis that would be required for some issues. Chapter 9 on CO_2 sequestration is simply disappointing. The proposed "mechanisms" of CO_2 trapping are accepted at face value, and there is no discussion of geochemical processes that would address some of the key challenges related to CO_2 injection into geological media and to perturbations in the carbonate system and their consequences for ion partitioning. While chapter 10 is a good introduction to the applications of aqueous solution–solid solution thermodynamics to the disposal of nuclear waste, the reader will find a more thorough discussion of the subject in reference 3.

Some of the challenges we identified in our previous book remain unanswered, particularly the one concerning the identification of key processes at the molecular and atomic levels. These processes should constitute the basis for any firm understanding and quantification of the mechanisms and thermodynamics of ion partition processes at ambient temperatures.

In essence, this is a useful book for anyone interested in low-temperature geochemistry, particularly as it relates to the carbon and sulphur cycles and trace element interactions.

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REFERENCES

1 Prieto M, Stoll H (eds) (2011) Ion Partitioning in Ambient-Temperature Aqueous Systems. EMU Notes in Mineralogy 10, ISBN is 978-0903056-26-7, 420 pp

2 Broecker WS (1985) How to Build a Habitable Planet. Columbia University Trustees, 291 pp

3 Bruno J, Bosback, Kulik D, Navrotsky A (2007) Chemical Thermodynamics of Solid Solutions of Interest in Nuclear Waste Management. OCDE Nuclear Energy Agency Data Bank, North-Holland Elsevier Science Publishers