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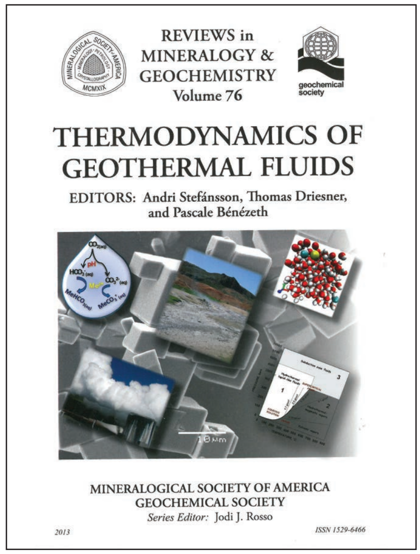
Book Review

Book Review: Thermodynamics of Geothermal Fluids, RIMG Volume 76. Edited by Andri Stefánsson, Thomas Driesner, and Pascale Bénézeth (2013) Reviews in Mineralogy and Geochemistry, i–x + 350 p., ISBN 978-0-939950-91-1.



This volume, edited by Andri Stefánsson, Thomas Driesner, and Pascale Bénézeth, is an extended review of the topics covered at the "Thermodynamics of Geothermal Fluids" short course held on August 24–25, 2013, prior to the 23rd Goldschmidt Conference in Florence, Italy. It is comprised of 9 chapters written by 22 authors. The book covers all domains of geothermal fluids, from subduction-mantle settings to surficial volcanic fumaroles. The references at the end of each chapter are an invaluable resource to further deepen the reader's knowledge.

Chapter 1 gives a general introduction to the volume and prepares the reader for the topic of "Thermodynamics of Geothermal Fluids" by presenting the subject, possible applications, and hurdles that still need to be investigated. Thermodynamic models play a central role in quantifying various processes that involve geothermal fluids, from geochemical studies, petroleum exploration, and ore deposition. With respect to CO_2-sequestration geothermal fluids are also important in questions regarding climate change.

Chapter 2 introduces the molecular-scale view of thermodynamics as it relates to geothermal fluids. Molecular-scale processes and macroscopic thermodynamic properties have a basic relationship whereby parameterizations of molecular interactions are used in numerical simulation techniques (e.g., Monte Carlo simulation). In several steps, the reader is introduced to the basic concept of statistical thermodynamics and how thermodynamic properties are derived and used in quantifying models. The chapter explains the three most established molecular simulations namely Monte Carlo (MC), molecular dynamics (MD), and ab-initio molecular dynamics (AIMD). Since the speciation of the fluids' molecules influence their dynamics, the last part of the chapter is dedicated to the processes involved in the hydration of ions. Experimental work on ion hydration has been mainly undertaken at low-pressure and -temperature conditions, which are not comparable to geothermal fluids. Accordingly, the authors stress the necessity of experiments at near- and supercritical regions to parametrize the models properly.

Chapter 3 ties onto the previous chapter by going deep into the thermodynamics of aqueous species, presenting equations of state (EoS) and transport theory. The authors start by describing basic thermodynamic models and comparing electrostatic models [e.g., the Helgeson-Kirkham-Flowers (HKF) model] as well as density models. The latter are successful in predicting the solubility of rock-forming minerals in aqueous fluids up to 2 GPa and 1100 °C. The chapter closes with applications of aqueous thermodynamics (e.g., geothermal systems) and the estimations of fluid fluxes. All models are underlain by a plethora of equations, adding up to 130 in total for the chapter.

Chapter 4 uses the example of the carbonate system to demonstrate mineral solubility in hydrothermal conditions to 300 °C. Carbon is omnipresent in geochemical processes from the mantle to the atmosphere whereby it shows a high speciation. In the form of CO_2, it is also a strong greenhouse gas and the main cause of man-made climate change. CO_2-sequestration is one of many possible applications where thermodynamic models are applicable. The authors explain common techniques for experiments on hydrothermal conditions and in-situ measurements of pH at various pressure and temperature conditions. The last part of the chapter focuses on the speciation and thermodynamic stabilities of carbon-bearing fluids at varying conditions and presents solubilities and mineralization processes of the most important carbonate phases.

Chapter 5 examines thermodynamics of fluid-rock interaction from mid-crustal to upper-mantle conditions by explaining

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various electrostatic, density, and activity models. Experimental and calculated mineral solubilities are compared to recent studies provide growing data of conditions at high pressure and temperature that are comparable to deep crust and upper mantle levels. The chapter closes with an investigation of mineral solubilities in saline fluids, demonstrating that Cl is an important ligand in hydrous fluids at high pressure and temperature.

Chapter 6 provides insight into the transport of metals and metalloids by geological vapors. The authors present the metal ion concentrations of aqueous solutions and their speciation. Experiments are compared with measurements of natural samples and the effects of ligands on element-partitioning of metalloids, alkali metals, and metals at the vapor-liquid interchange are shown. The chapter continues with the comparison of different geothermal systems and discusses phase separation of fluid and vapors as well as post-entrapment modifications of fluid inclusions.

Chapter 7 gives insight into the state-of-the-art of solution calorimetry under hydrothermal conditions. It starts with the introduction of thermodynamic relations and the equation of state for standard partial molar properties and standard partial molar heat capacities. The major part of this chapter covers the various instruments used in densimetry, heat-capacity calorimetry, and heat of mixing calorimetry. The authors point to the need of experiments at temperatures >100 °C to the supercritical region in order to collect data for electrolytes and non-electrolytes for thermodynamic models.

Chapter 8 describes the structure and thermodynamics of subduction zone fluids as shown from spectroscopic studies. Subduction zone fluids comprise a broad geochemistry depending on pressure and temperature, whereby the amount of total dissolved solids (TDS) increases with depth but, generally, stays at very low levels. The chapter carries on by discussing the polymerization of silica and alkali aluminosilicate components that change with pH, pressure, and temperature. Thereafter, various in-situ spectroscopic methods are presented that focus on the speciation and mobilization of rare earth elements (REE) and high field strength elements (HFSE). The authors describe experimental methods and spectroscopic analyses of fluid-inclusions and in-situ from diamond-anvil cell (DAC) experiments. The chapter closes with the discussion of water activity in saline solutions and the effect of the dissolved ions on the depth of dehydration.

Last, Chapter 9 examines the thermodynamics of organic transformations in hydrothermal fluids. Organic contents are diversely found in geothermal fluids ranging from hydrothermal vents deep in the ocean to bituminous liquids that are involved in the formation of petroleum. The chapter starts with an inventory of organic compounds in hydrothermal fluids and the techniques that are used to determine the carbon speciation. The formation of petroleum in the "oil window" is explained by the incongruent melting of immature kerogen. The authors also show how heavy metals like uranium are reduced and enriched in anoxic sediments due to the oxidation of organic matter. Oxidation-reduction and hydration-dehydration reactions are explained in the context of how they are coupled with the formation of metal oxides. The last part describes experimental studies on reversible and irreversible reactions and points to the need of further investigation on the processes that lead to bond breakage between hydrogen and carbon.

The whole volume provides a good insight into the field of fluid thermodynamics and contains a plethora of equations and references for further reading. All chapters give a brief introduction before going into more detailed explanations. The book is suitable for postgraduate studies since it assumes prior knowledge of basic thermodynamic processes. I recommend this book from my background as an experimental petrologist, and it was very helpful in understanding fluid-driven processes in sub-solidus experiments.

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Department of Earth and Planetary Sciences
Macquarie University
Sydney, New South Wales 2109
Australia

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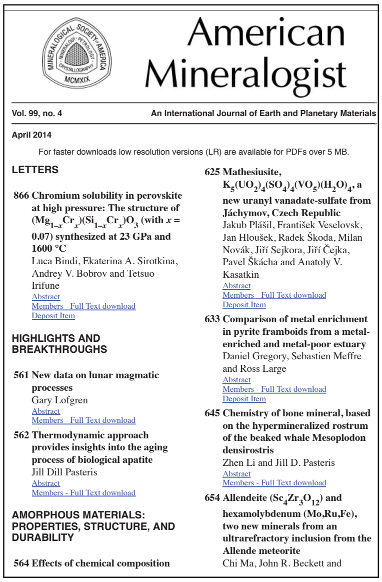

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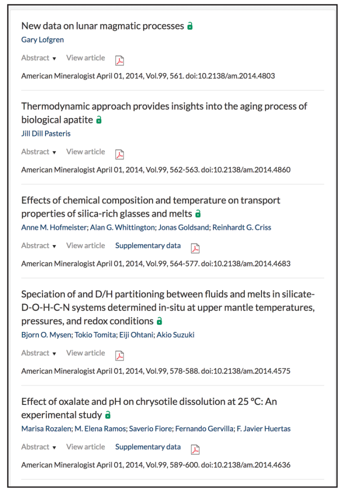

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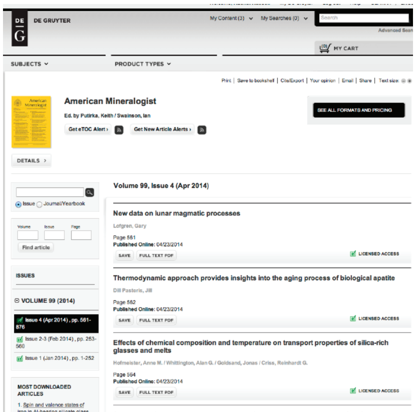

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