DEVELOPMENTS IN SEDIMENTOLOGY 62

CARBONATES IN CONTINENTAL SETTINGS

GEOCHEMISTRY, DIAGENESIS AND APPLICATIONS

EDITED BY

A.M. ALONSO-ZARZA & L.H. TANNER

SERIES EDITOR: A. J. VAN LOON

VOLUME SIXTY TWO

DEVELOPMENTS IN SEDIMENTOLOGY

CARBONATES IN CONTINENTAL SETTINGS: GEOCHEMISTRY, DIAGENESIS AND APPLICATIONS

Editors

A.M. Alonso-Zarza
Dpto Petrología y Geoquímica,
Fac. CC. Geológicas, IGE-CSIC, Universidad
Complutense de Madrid, Madrid, Spain

and

L.H. Tanner
Department of Biological Sciences,
Le Moyne College, Syracuse, NY, USA

ELSEVIER
Amsterdam • Boston • Heidelberg • London • New York • Oxford
Paris • San Diego • San Francisco • Singapore • Sydney • Tokyo

Elsevier
Radarweg 29, PO Box 211, 1000 AE Amsterdam, The Netherlands
Linacre House, Jordan Hill, Oxford OX2 8DP, UK

First edition 2010

Copyright © 2010 Elsevier B.V. All rights reserved

No part of this publication may be reproduced, stored in a retrieval system or transmitted in any form or by any means electronic, mechanical, photocopying, recording or otherwise without the prior written permission of the publisher

Permissions may be sought directly from Elsevier's Science & Technology Rights Department in Oxford, UK: phone (+44) (0) 1865 843830; fax (+44) (0) 1865 853333; email: permissions@elsevier.com. Alternatively you can submit your request online by visiting the Elsevier web site at http://www.elsevier.com/locate/permissions, and selecting *Obtaining permission to use Elsevier material*

Notice
No responsibility is assumed by the publisher for any injury and/or damage to persons or property as a matter of products liability, negligence or otherwise, or from any use or operation of any methods, products, instructions or ideas contained in the material herein. Because of rapid advances in the medical sciences, in particular, independent verification of diagnoses and drug dosages should be made

British Library Cataloguing in Publication Data
A catalogue record for this book is available from the British Library

Library of Congress Cataloging-in-Publication Data
A catalog record for this book is available from the Library of Congress

ISBN: 978-0-444-53526-9
ISSN: 0070-4571

For information on all Elsevier publications
visit our website at elsevierdirect.com

Printed and bound in Great Britain

10 11 12 13 14 10 9 8 7 6 5 4 3 2 1

Working together to grow
libraries in developing countries

www.elsevier.com | www.bookaid.org | www.sabre.org

ELSEVIER BOOK AID International Sabre Foundation

VOLUME SIXTY TWO

DEVELOPMENTS IN SEDIMENTOLOGY

CARBONATES IN CONTINENTAL SETTINGS: GEOCHEMISTRY, DIAGENESIS AND APPLICATIONS

CONTRIBUTORS

Ildefonso Armenteros
Departamento de Geología, Facultad de Ciencias, Universidad de Salamanca, 37017 Salamanca, Spain

Maria Angeles Bustillo
Museo Nacional de Ciencias Naturales-CSIC, C/José Gutiérrez, Abascal 2, 28006 Madrid, Spain

Daniel M. Deocampo
Department of Geosciences, Georgia State University, P.O. Box 4105, Atlanta, GA 30302, USA

J.I. Escavy
Lafarge Cementos, C. Isaac Newton s/n, 46500 Sagunto, Spain

Debra L. Hanneman
Whitehall Geogroup, Inc., 107 Whitetail Road, Whitehall, MT 59759, USA

M.J. Herrero
Departamento de Petrología y Geoquímica, Universidad Complutense, C. José Antonio Novais 2, 28040 Madrid, Spain

Allan Pentecost
The Freshwater Biological Association, Ferry Landing, Sawrey, Cumbria, LA22 0LP, UK

Lawrence H. Tanner
Department of Biology, Le Moyne College, 1419 Salt Springs Road, Syracuse, NY 13214, USA

Charles J. Wideman
Emeritus, Montana Tech of the University of Montana, Butte, MT 59701, USA

PREFACE

In this, the second volume of the two-volume review of carbonates in continental settings, we continue our survey of the important aspects of their formation and utilisation. Whereas the first volume emphasised the formation of carbonate sediments, covering the depositional settings, facies and sedimentological processes; this second volume examines the geochemistry, diagenesis, sequence stratigraphy of these deposits, along with some of the practical applications.

The geochemistry of continental carbonates is discussed in depth in Chapter 1. The controls on the precipitation of inorganic carbonates and the resultant geochemical composition are analysed in the first part of the chapter, whereas applications of isotope geochemistry and the systematics of the geochemistry of a wide variety of carbonate deposits are covered later in the chapter.

Chapters 2 and 3 focus on the diagenesis of continental carbonates. Chapter 2 presents an extensive review of the carbonate-related diagenetic processes that affect these deposits, including cementation, neomorphism, dolomitisation and dedolomitisation, amongst others, in eogenetic, burial and telogenetic environments. The silicification of continental carbonate is specifically analysed in Chapter 3; the different diagenetic environments (meteoric vs. burial) as well as the isotopic signal of continental cherts are considered here.

Chapters 4 and 5 provide an overview on major uses of carbonates for the large-scale studies of sedimentary basins. The use of continental carbonates as palaeoclimatic archives is the aim of Chapter 4, in which each type of carbonate and the different macro- and micromorphological features, as well as geochemical (including isotopic) palaeoclimatic indicators are described. Chapter 5 provides an extensive overview on the principles and applications of sequence stratigraphy in continental basins containing carbonates.

There is certainly great economic interest in continental carbonates, as they have many practical uses, such as building material, and as source and/or host rocks for deposits of gas, oil and coal. These wide economic applications of continental carbonates are presented in Chapter 6. Finally, continental carbonates form in very fragile and sensitive environments, and in many cases their formation creates spectacular landscapes that are considered significant natural sites. The formation and conservation of these sites is the topic of the last chapter of this volume.

We hope that the reader, whether student or researcher, finds the information provided in both of these volumes both stimulating and informative. Ideally, these chapters will provide a base for understanding the importance of continental carbonates and serve as a starting point for adding to this knowledge.

Once again, we would like to thank the reviewers who dedicated their time, and in so doing, made this volume possible. We were truly lucky to have had the help of the following colleagues: P. Anadón, C. Arenas, Ll. Cabrera, F. McDermott, D. Deocampo, S. Dunagan, B. Jones, D. Larsen, M. Pedley, R. Renaut, B.P. Singh, R. Sinha, N. Tabor and L. Tapanila. Our sincere thanks also go to our families and our departments: Departamento de Petrología y Geoquímica de la Universidad Complutense, IGE-CSIC, de Madrid, the Department of Biological Sciences at Le Moyne College. Lastly, producing this volume would not have been possible without the assistance of the book series editor, A.J. (Tom) van Loon, of Adam Mickiewicz University, Poznan.

A.M. Alonso-Zarza
L.H. Tanner
Editors

CONTENTS

CHAPTER 1

THE GEOCHEMISTRY OF CONTINENTAL CARBONATES

Daniel M. Deocampo*

Contents

1. INTRODUCTION

Non-clastic carbonates form an important class of sediment, having precipitated from solution either through inorganic precipitation or through a biologically mediated process. Throughout the sedimentary record of the earth, they comprise an important component of continental sediments, providing insights into paleoenvironmental, paleoecological, and paleoclimatic conditions. Analyses of elemental and isotopic geochemistry are now fundamental to any study of carbonate deposits, subject to the many

---

*Corresponding author.
E-mail address: deocampo@gsu.edu

Department of Geosciences, Georgia State University, P.O. Box 4105, Atlanta, GA 30302, USA

Developments in Sedimentology, Volume 62
ISSN 0070-4571, DOI 10.1016/S0070-4571(09)06201-3

complexities introduced by the sensitivity of carbonate minerals to early, middle, and late diagenetic alteration.

The precipitation of carbonate minerals from continental water is fundamentally controlled by the thermodynamics of the carbonate mineral systems. Even given the dramatic importance of biota in mediating mineral precipitation reactions, such organisms must somehow achieve mineral supersaturation in order for biomineralization to occur, either within or near cellular tissue (e.g., the proton pump of Lian et al., 2006). Understanding the geochemistry of carbonate minerals, therefore, is fundamentally a question of understanding ionic activities in solution at the time of precipitation.

Despite the simplicity of the thermodynamics, however, carbonate mineral precipitation in near-surface continental environments is tremendously complicated by the geochemical impacts of large and small organisms, and reaction kinetics in an environment with non-ideal ion interactions, variable substrates, fluctuating pH, organic molecules, and gas phase interactions. With these complications in mind, it is nevertheless helpful to consider that, when we observe sedimentary carbonates, the fundamental reason that solid calcite, for example, exists is because $\mathrm{Ca}^{2+}_{(aq)}$ and $\mathrm{CO}^{2-}_{3(aq)}$ were present in sufficient concentrations and activities for calcite to be supersaturated. Hence, a lack of calcareous microfossils in a lacustrine deposit may be directly due to limnological processes inhibiting the bioavailability of $\mathrm{Ca}^{2+}_{(aq)}$, rather than to other ecological factors such as pH or salinity. Understanding the genesis of carbonate minerals, therefore, is a question of understanding what processes promote supersaturation and precipitation (Table 1), be they biotic or abiotic, and what kinetic effects inhibit precipitation (perhaps favoring certain phases). Moreover, understanding how these processes control the incorporation and partitioning of major and trace elements, and stable isotopes (especially of C, O, and Sr) provides a powerful tool for paleoenvironmental reconstruction.

The purpose of this chapter is to provide a broad review of the geochemistry of continental carbonates, with emphasis on the development of the sedimentary record. This is a tremendous field, represented by an enormous body of literature. In some ways, the continental sedimentologists of today who work with carbonates face many of the challenges confronting marine geologists of past decades, where fundamental concepts such as reaction kinetics and biogeochemical effects remain problematic and difficult to quantify in the field. Indeed, some problems, such as the "dolomite problem," are common to both marine and continental sediments. Nevertheless, this chapter attempts to summarize the key aspects of geochemistry relevant to continental sediments. The chapter is organized into first a discussion of the major element geochemistry of waters from which inorganic carbonates are commonly precipitated, and the resulting elemental geochemistry observed in carbonates, especially in lakes. Then the controls on isotopic composition of carbonates are discussed, with examples from lacustrine,

Table 1 Names, chemical formulas, and *K* values for major carbonate minerals.

Name	Chemical formulas	$\log K_{25}$ (disordered, if available)	References
Calcite	$CaCO_3$	−8.48	(1)
Aragonite	$CaCO_3$	−8.34	(1)
Vaterite	$CaCO_3$	−7.91	(1)
Monohydrocalcite	$CaCO_3 \cdot H_2O$	−7.15	(2)
Dolomite	$CaMg(CO_3)_2$	−17.09 (−16.54)	(3)
Ikaite	$CaCO_3 \cdot 6H_2O$	−6.62	(4)
Huntite	$CaMg_3(CO_3)_4$	−29.97	(3)
Magnesite	$MgCO_3$	−8.03	(3)
Hydromagnesite	$4(MgCO_3) \cdot Mg(OH)_2 \cdot 4H_2O$	−8.76	(3)
Nesquehonite	$MgCO_3 \cdot 3H_2O$	−5.62	(3)
Trona	$Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$	−0.80	(3)
Thermonatrite	$Na_2CO_3 \cdot H_2O$	0.13	(3)
Nahcolite	$NaHCO_3$	−0.55	(3)
Natron	$Na_2CO_3 \cdot 10H_2O$	−1.31	(3)
Pirssonite	$CaCO_3 \cdot Na_2CO_3 \cdot 2H_2O$	−9.23	(5)
Gaylussite	$CaCO_3 \cdot Na_2CO_3 \cdot 5H_2O$	−9.42	(5)
Kalicinite	$KHCO_3$	−10.06	(5)
Siderite	$FeCO_3$	−10.89	(3)
Malachite	$Cu_2(OH)_2CO_3$	5.15	(3)
Azurite	$Cu_3(OH)_2(CO_3)_2$	3.75	(3)
Smithsonite	$ZnCO_3 \cdot H_2O$	−10.0	(3)
Rhodacrosite	$MnCO_3$	−11.43 (−10.39)	(3)
Cerussite	$PbCO_3$	−13.13	(3)
Strontianite	$SrCO_3$	−9.27	(6)
Witherite	$BaCO_3$	−8.56	(3)
Burkeite	$Na_2CO_3 \cdot 2Na_2SO_4$	−0.772	(3)

Sources: (1) Plummer and Busenberg (1982); (2) Kralj and Brecevic (1995); (3) Ball and Nordstrom (1991); (4) Clarkson et al. (1992) (5) Plummer et al. (1988) (6) Busenberg et al. (1984).

pedogenic, tufa, and karst carbonates. The chapter then discusses saline carbonates common to evaporative environments and, finally, ostracodes, perhaps the most common carbonate lacustrine microfossil used in paleolimnology.

2. PRECIPITATION OF INORGANIC CARBONATES

The dissolved constituents that contribute to carbonate minerals are chiefly calcium, magnesium, and carbonate. The concentration of other solutes is also an important factor, as total salinity can affect ion interactions; the net balance of conservative cations and anions is a principal factor in determining alkalinity (Drever, 1997), and minor and trace elements are also incorporated into carbonate crystals. As with the other solutes, the alkaline earths (Ca and Mg) in dilute surface waters are derived principally from atmospheric input and chemical weathering. Weathering reactions contributing alkaline earths to surface waters are principally dissolution of salts or carbonates, or hydrolysis of aluminosilicate minerals (Jones and Deocampo, 2003). Whereas these reactions are the ones which release the alkaline earths into solution, other mineral reactions can have important impacts on dissolved CO_2. For example, the oxidation of sulfide minerals (e.g., pyrite) will contribute dissolved sulfate, increasing the balance of anions and inhibiting dissolution of CO_2, thereby reducing dissolved inorganic carbon.

The water/rock interactions that lead to the acquisition of alkalinity in dilute waters are critical to the later geochemical evolution of those waters, especially in catchment areas where evaporation exceeds precipitation. As shown by Hardie and Eugster (1970), the initial ratio of Ca^{2+} to HCO_3^- in dilute waters determines which of these solutes will be effectively eliminated by subsequent precipitation of calcite. Indeed, because of its relatively lower solubility, calcite forms the first of several such "chemical divides" that have the potential to dramatically lower individual solute concentrations in evaporatively enriched waters; in this case, calcite can precipitate as long as Ca^{2+} and CO_3^{2-} are available. Once the concentration of one of the two is sufficiently lowered, the mineral can no longer precipitate and the other solute begins to accumulate in the water again. The solute ratios produced by atmospheric input and weathering are therefore very important in determining later solution chemistries. They are largely a product of catchment-area lithology, with carbonate favored by volcaniclastics and mafic silicate rocks, alkaline earths favored by sulfide-bearing rocks (e.g., shale), and rough equality achieved in limestone terrains (Jones and Deocampo, 2003).

Perhaps volumetrically the most significant continental carbonates are those authigenic carbonates formed in lacustrine basins. Notwithstanding the complexities of distinguishing inorganic from biogenic carbonates, precipitation mechanisms that are largely abiotic are instructive in helping us understand the processes at work. In consideration of the geochemistry of inorganic lacustrine carbonates, the Mg/Ca ratio in the water is an important control on both mineralogy and the Mg content of carbonates. In order for inorganic carbonates to precipitate at all, concentrations of Ca^{2+} and CO_3^{2-} must be elevated to the point that supersaturation is reached. At 25°C and 1 atm pressure, thermodynamic equilibrium for calcite is expressed as

$$\alpha_{Ca^{2+}}\alpha_{CO_3^{2-}} = K_{\text{calcite}} = 10^{-8.48} \tag{1}$$

where α refers to the activity of the ion, generally some fraction of the ion's concentration, and K the thermodynamic constant for the mineral (Drever, 1997). When the ion activity product for calcite is greater than K_{calcite}, the mineral is supersaturated. For this to occur, high levels of Ca^{2+}, CO_3^{2-}, or both are required. This occurs easily with evaporative concentration, and Garrels and Mackenzie (1967) showed in model studies of evaporated waters of the Sierra Nevada that very little evaporative concentration is required to produce calcite saturation. The equilibrium expression for aragonite is identical, with a slightly higher solubility (Drever, 1997)

$$\alpha_{\mathrm{Ca}^{2+}}\alpha_{\mathrm{CO}_3^{2-}} = K_{\mathrm{aragonite}} = 10^{-8.34} \tag{2}$$

As discussed below, however, aragonite tends to form only in more evaporatively evolved waters, with high Mg/Ca ratios. For crystalline dolomite, the equilibrium expression changes slightly to

$$\alpha_{\mathrm{Ca}^{2+}}\alpha_{\mathrm{Mg}^{2+}}\alpha^{2}_{\mathrm{CO}_3^{2-}} = K_{\mathrm{dolomite}} = 10^{-17.2} \tag{3}$$

(Sherman and Barak, 2000). Of course, even in waters that are supersaturated with respect to dolomite, kinetic effects often inhibit precipitation, as discussed further below.

A second common mechanism that induces the precipitation of inorganic carbonates is through the elevation of CO_3^{2-} due to pH changes. Dissolved inorganic carbon can be thought of as dissolved carbon dioxide, but it behaves as a weak acid (Drever, 1997). When CO_2 initially dissolves, it forms the weak acid $\mathrm{H}_2\mathrm{CO}_3$. The pH of the water determines the overall state of protonation of the carbonic acid: $\mathrm{H}_2\mathrm{CO}_3$ dominates low-pH waters, HCO_3^- dominates circum-neutral waters, and CO_3^{2-} is the dominant form only in very high-pH waters. Ultimately, CO_3^{2-} is related to pH and P_{CO_2} according to the following relationship:

$$\alpha_{\mathrm{CO}_3^{2-}} = P_{\mathrm{CO}_2}K_{\mathrm{H}}K_1K_2\alpha_{\mathrm{H}^+} \tag{4}$$

where $K_{\mathrm{H}} = 10^{-1.5}$ (Henry's Law constant governing dissolution of CO_2), and the dissociation constants of carbonic acid are $K_1 = 10^{-6.35}$ and $K_2 = 10^{-10.33}$ (Drever, 1997). Thus, changes in P_{CO_2} or pH have a direct impact on the ion activity product for carbonates (Equations (1)–(3)). These mass–balance relationships are the fundamental controls on inorganic carbonate precipitation.

Biotic processes are often important contributors to the saturation state of carbonates. For example, photosynthesis by aquatic organisms can draw down dissolved CO_2 levels, leading to a pH rise; conversely, respiration releases CO_2, depressing pH (Deocampo and Ashley, 1999). A common misconception is that photosynthesis or respiration changes alkalinity; in fact, alkalinity is conservative during these reactions, with charge balance being achieved by CO_2 equilibria. See Marion (2001) and De Visscher and Vanderdeelen (2003) for a more detailed discussion of the thermodynamics of the carbonate system, especially in waters with somewhat elevated ionic strengths requiring special consideration of ion interactions.

As calcite precipitates due to evaporative concentration or another forcing mechanism, the first calcites to precipitate are generally those with little or no Mg content. High dissolved Mg is required for Mg-bearing carbonates to precipitate, but the Mg/Ca ratios in the waters are generally low at this early stage. As calcite precipitates, however, Ca^{2+} is quantitatively lost from solution, even as evaporative concentration and continued inflow increase the concentrations of other solutes. Therefore, the Mg/Ca ratio increases as calcite precipitation proceeds. In the absence of substantial recharge, progressive calcite precipitation leads to higher solution Mg/Ca ratios and therefore Mg-bearing carbonates. This is likely the most common way for Mg/Ca ratios to become elevated, hence the overwhelming tendency for Mg-rich carbonates, such as dolomite and magnesite, to occur nearly exclusively in evaporatively concentrated lakes (Müller et al., 1972; Last, 1990). Exceptions include those environments with actively weathering high-Mg rocks, such as the Amboseli Basin, Kenya, where Mg-rich volcanics are being weathered (Hay et al., 1995), dolostone terrains (Alonso-Zarza and Martín-Pérez, 2008), and microbially induced precipitation such as in sulfate-reducing microbial communities as discussed below (e.g., Vasconcelos and McKenzie, 1997).

The geochemical effects of carbonate precipitation can be seen well through the use of ternary plots, such as a "Spencer Triangle" (Figure 1) with equivalents of Ca^{2+}, SO_4^{2-}, and ($HCO_3^-+CO_3^{2-}$) on the vertices (Smoot and Lowenstein, 1991; Spencer, 2000). As pure calcium carbonate precipitates, the position of a solution on the ternary diagram will migrate directly away from the calcite point on the $Ca^{2+}-(HCO_3^-+CO_3^{2-})$ axis, which is exactly halfway between the vertices representing 50% composition of each. If Ca^{2+} is exhausted before carbonate, then the solution chemistry approaches the $SO_4-(HCO_3^-+CO_3^{2-})$ axis; this case is predicted for simple evaporation of "World River" water (composition from Livingstone, 1963). If Ca^{2+} is in excess of carbonate, but less than SO_4^{2-}, the water first migrates to the $SO_4^{2-}-Ca^{2+}$ axis; subsequent precipitation of gypsum forces it to the SO_4^{2-} vertex, as in evaporated Tule Spring (Death Valley, California) waters (Jones and Bodine, 1987) or evaporated seawater. If Ca^{2+} is in excess of both other constituents, then gypsum precipitation forces water compositions to the Ca^{2+} vertex, which is where Mid-Ocean Ridge hydrothermal fluids plot (Jones and Deocampo, 2003). This is an unusual geochemistry, and a good indicator of hydrothermal contribution to the basin, such as in the Qaidam Basin of China (Spencer et al., 1990). Eventually, evaporative concentration of such Ca-rich waters may produce deposits of antarcticite ($CaCl_2$) (Jones and Deocampo, 2003).

A second ternary diagram termed the "Jones" triangle can be plotted with Mg^{2+}, SO_4^{2-}, and $HCO_3^-+CO_3^{2-}$ on the vertices (Figure 2) (Jones and Deocampo, 2003). Most dilute surface waters would plot near the lower right corner of the triangle, with carbonate tending to dominate over both

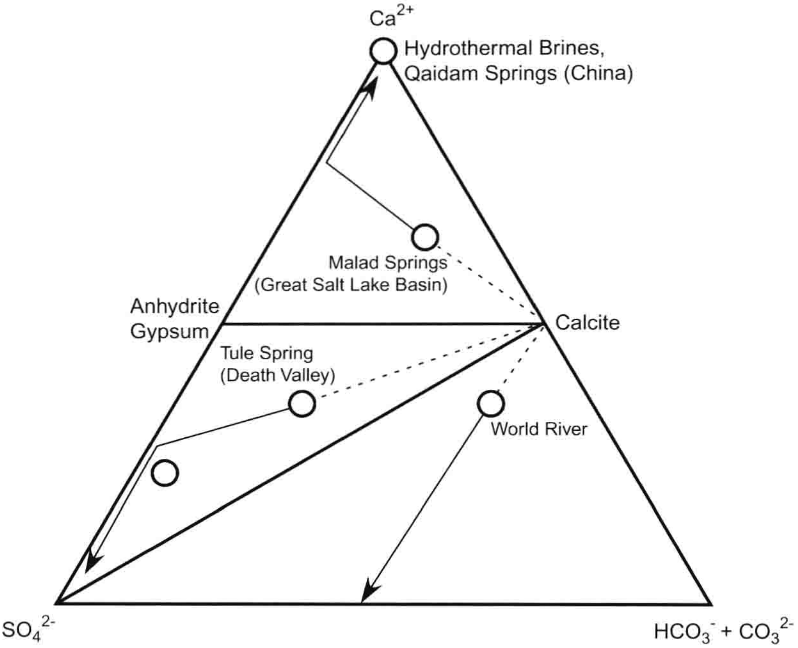

Figure 1 Ternary diagram ("Spencer Triangle") depicting molar ratios of solutes (Smoot and Lowenstein, 1991; Spencer, 2000). Precipitation of calcite forces solution chemistry to migrate away from the Calcite midpoint between Ca and HCO_3+CO_3. Subsequent precipitation of gypsum drives solution chemistry toward the upper or lower left vertex.

calcium and sulfate for typical meteoric waters. As calcite precipitates, the solution composition will migrate directly away from the lower right corner, as CO_3^{2-} is quantitatively lost compared to Mg^{2+} and SO_4^{2-}. The distance away from the CO_3^{2-} corner that the solution composition migrates on this trajectory depends on how rapidly the solution's Mg^{2+}/Ca^{2+} ratio increases. If Ca^{2+} is rapidly depleted, driving Mg^{2+}/Ca^{2+} up quickly, then Mg-rich carbonates can be produced fairly early during evaporative concentration; if more calcite can be produced without exhausting Ca^{2+}, then Mg^{2+}/Ca^{2+} ratios go up later, once the solution chemistry has migrated farther from the CO_3^{2-} corner. The timing of the Ca^{2+} depletion therefore has important implications for (1) the total salinity at which Mg-rich carbonates may precipitate and (2) the resulting Mg^{2+}/SO_4^{2-} and SO_4^{2-}/CO_3^{2-} ratios in the residual fluid. Evidence for calcite precipitation altering lacustrine water Mg/Ca is clearly seen in a longitudinal evaporative system such as Lake Balkash, Kazakhstan (Verzilin et al., 1991; Petr, 1992). Lake water Mg^{2+}/Ca^{2+} ratios near the freshwater Ili River input are ~1.0. Some 800 km down the hydraulic gradient to the