Chemical Geology 296-297 (2012) 50–65

Contents lists available at SciVerse ScienceDirect

Chemical Geology

journal homepage: www.elsevier.com/locate/chemgeo

Research paper

Influences on the carbonate hydrochemistry of mound spring environments, Lake Eyre South region, South Australia

Mark N. Keppel [a,*], Vincent E.A. Post [b], Andrew J. Love [a], Jonathan D.A. Clarke [c], Adrian D. Werner [a,b]

[a] School of the Environment, Flinders University, GPO Box 2100, Adelaide, South Australia 5001, Australia
[b] National Centre for Groundwater Research and Training, Flinders University, GPO Box 2100, Adelaide, South Australia 5001, Australia
[c] The Mars Society Australia, P.O. Box 327, Clifton Hill, Victoria 3068, Australia

ARTICLE INFO

Article history:
Received 29 March 2011
Received in revised form 18 December 2011
Accepted 21 December 2011
Available online 30 December 2011

Editor: U. Brand

Keywords:
Tufa
Hydrochemistry
Great Artesian Basin
Mound springs
South Australia

ABSTRACT

Mound spring structures composed of tufa precipitated from near-ambient temperature spring waters are rare; consequently, the hydrochemical evolution of the water and the processes that control carbonate deposition in these systems are not well understood. This study analysed the water from 3 mound springs in an arid environment in the vicinity of Lake Eyre South, South Australia. Samples were tested for major ion chemistry and stable isotope ratios of water ($^{2}H/^{1}H$ and $^{18}O/^{16}O$). Most CO_2 degasses from water (i) before emergence as it ascends in the fracture-derived spring conduit system below the spring opening and (ii) after emergence in the turbulent upper tail environment between the spring vent pool and the tail delta. However, modern carbonate precipitation was generally restricted to tail delta environments, spatially disconnected from the areas of strongest CO_2-degassing. In addition to CO_2-degassing and carbonate precipitation, evapotranspiration and heterotrophy were inferred to be processes controlling the chemical evolution of water flowing through the tail delta. Based on considerations of the geometry of the tail delta and evapotranspiration rates, it was inferred that infiltration is an important process in determining the tail delta size and hence the morphology of the mound spring environment. A reactive transport model was used to assess the importance of these processes for the evolution of carbonate hydrochemistry. The model outcomes showed that water loss via evapotranspiration does not significantly affect tufa precipitation, despite the springs being located within an arid environment. Heterotrophy was considered in the model in order to reproduce observed pH and carbonate concentrations, highlighting the role of vegetation in controlling the water chemistry. The modelling approach adopted here provides a generic framework for the analysis of calcareous spring deposits and places quantitative constraints on data-based process conceptualisation.

1. Introduction

Calcareous spring deposits are limestones precipitated from spring water (Jones and Renaut, 2010). As the fabric, mineralogy and geochemistry of these rocks are sensitive to the particular environmental conditions in which they form, these deposits can be important archives of information concerning palaeo-environmental conditions and have consequently been studied to understand the palaeohydrology, palaeoclimatology and neotectonics of regions where they occur (e.g. Hancock et al., 1999; Andrews, 2006; Miner et al., 2007; Love et al., 2009). However, adequate interpretation requires that the factors and processes that control the structure and morphology of these deposits are well understood.

Calcareous spring deposits in the vicinity of Lake Eyre South in South Australia are often dome-shaped and are associated with spring water discharge from the Great Artesian Basin (GAB). These morphological features are locally known as “mound springs” (Habermehl, 1982). The precipitation of carbonate from emergent spring water and the controls on this process are integral to the construction of these morphological features. Similar structures found elsewhere in the world are often referred to as spring mounds (e.g. Crombie et al., 1997; Linares et al., 2010). The mound springs of the GAB hold great cultural, tourist and ecological importance (e.g. Ah Chee, 2002; Leek, 2002; Ponder, 2004) and their preservation has a high priority, which requires in-depth knowledge of their formation mechanisms.

Early works concerning the carbonate hydrochemistry of calcareous spring environments by Barnes (1965), Holland et al. (1964) and Langmuir (1971) identified CO_2-degassing as the main driver for carbonate precipitation and showed that calcite super-saturation occurs due to a difference in the physio–chemical conditions between the subsurface and the surface environment. Recently Shvartsev et al. (2007) determined that hydrolysis of aluminosilicates, producing

---

[*] Corresponding author. Tel.: +61 8 8201 5203; fax: +61 8 8201 3567.
E-mail addresses: mark.keppel@flinders.edu.au (M.N. Keppel), vincent.post@flinders.edu.au (V.E.A. Post), andy.love@flinders.edu.au (A.J. Love), jon.clarke@bigpond.com (J.D.A. Clarke), adrian.werner@flinders.edu.au (A.D. Werner).

0009-2541/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.chemgeo.2011.12.017

HCO_3^- and Ca^{2+} as by-products, was also capable of forming carbonate-precipitating spring waters. However, other processes and factors have been identified that simultaneously interfere with the formation process; Herman and Lorah (1987), Lebron and Suarez (1996), Liu et al. (1995), Meyer (1984), and Pentecost (1992) found that the calcite super-saturation does not necessarily lead to immediate precipitation as there may be kinetic inhibition. Other studies have explored the particular micro-environmental conditions that may promote precipitation in nature; for instance, Chen et al. (2004), Dreybrodt and Buhmann (1991), Kano et al. (1999), Liu et al. (1995), Lorah and Herman (1988), Lu et al. (2000) and Zhang et al. (2001) all found that turbulent flow conditions will promote CO_2-degassing by reducing pressure, increasing the water surface area and reducing the diffusion boundary layer in the stream, thereby increasing the rate of calcium carbonate ($CaCO_3$) precipitation. Likewise, some studies have argued that biological processes such as photosynthesis of microbial organisms affect the precipitation of $CaCO_3$, particularly in quiescent flow conditions. Such studies include Baskar et al. (2006), González-Muñoz et al. (2010), Lee (2003) and Pentecost (1988), who inferred the importance of biomineralisation by isolating particular microbes in a laboratory-based setting. Gradzinski (2010), Kandianis et al. (2008), Pedley and Rogerson (2010) and Pedley et al. (2009) drew similar conclusions via a number of experiments using natural surface waters. Macrophytes can impact calcareous spring deposits by providing additional substrate for the nucleation and accumulation of carbonate precipitate (Pedley, 1992; Pentecost, 2005) and can also affect water chemistry via photosynthesis (Spiro and Pentecost, 1991; Pentecost, 1992; Liu et al., 2006, 2008).

Carthew et al. (2003, 2006), Pedley et al. (1996), Pentecost (2005), Radke (1990) and Wright (2000) suggested that evaporation is an important factor in ambient-temperature calcareous spring deposition in semi-arid and arid environments, but hydrochemical data was not used in any of these studies to provide supporting evidence. The effect of flow conditions on carbonate precipitation has to date focused on the effects of turbulence, such as in waterfalls (e.g. Zhang et al., 2001; Chen et al., 2004) and barrages forming pool structures (e.g. Lu et al., 2000). Of most relevance to this study, Kerr and Turner (1996) grew mounds of sodium carbonate (Na_2CO_3) in a controlled laboratory environment, but the value of these experiments as a generic analogue for mound springs is limited by their design, notably the use of Na_2CO_3 rather than $CaCO_3$, and the temperature differential between "spring water" and ambient conditions, which is not necessarily encountered in actual field conditions.

Terminology used in the international literature to describe spring-related carbonates is diverse (Jones and Renaut, 2010); the nomenclature by Ford and Pedley (1996) has been adopted here. They defined "tufa" as a fine-grained micritic carbonate precipitated at ambient and sub-ambient water temperatures containing abundant microbial-influenced textures.

Many of the mound springs of the Lake Eyre South region are interpreted to be composed of tufa (Habermehl, 1986; Keppel et al., 2011). Despite previous references to GAB mound springs in the international literature (e.g. Williams and Holmes, 1978; Viles and Goudie, 1990; Ford and Pedley, 1996; Kerr and Turner, 1996; Mudd, 2000; Pentecost, 2005), there is little information on the hydrochemistry of these environments. The same holds for the few detailed studies of active environments of similar features found elsewhere in the world (Pentecost and Viles, 1994; Pentecost, 2005; Linares et al., 2010).

The lack of hydrochemical data concerning the active depositional environments of mound springs renders our current understanding of the processes that control the formation of these features limited. The purpose of this study is to determine the environmental or hydrochemical conditions affecting formation and ongoing evolution of mound springs. To this aim, water samples from a number of active spring environments in the Lake Eyre South region of South Australia were collected and a novel application of reactive transport modelling was developed for the delta-shaped spring discharge fans. Additionally, evapotranspiration effects were quantified by the use of chloride (Cl^-) and stable isotope analysis. Based on the data and the model simulations, the relative contributions of CO_2-degassing and evapotranspiration to $CaCO_3$ precipitation have been quantified.

2. Study area

2.1. Climate and hydrology

The study area is situated in an arid climate zone within the southwestern corner of the Lake Eyre Basin. The mean daily maximum temperature for the nearest town with records (Marree, Fig. 1) is 28.4 °C, whereas the mean daily minimum temperature is 13.3 °C. The average annual rainfall is approximately 125 mm/yr. Rainfall totals between given years can vary significantly and are predominantly in the form of sporadic weak winter-dominated (June to August) weather events (Allan, 1990; McMahon et al., 2005). Pan evaporation rates for the Cooper Creek region of central Australia average 2.5 m/yr (Hamilton et al., 2005).

Regional drainage is directed predominantly to the east towards Lake Eyre South. A small but continuous contribution to stream flow is provided by spring waters supplied by the GAB. Stream flow events derived from precipitation are infrequent (Allan, 1990).

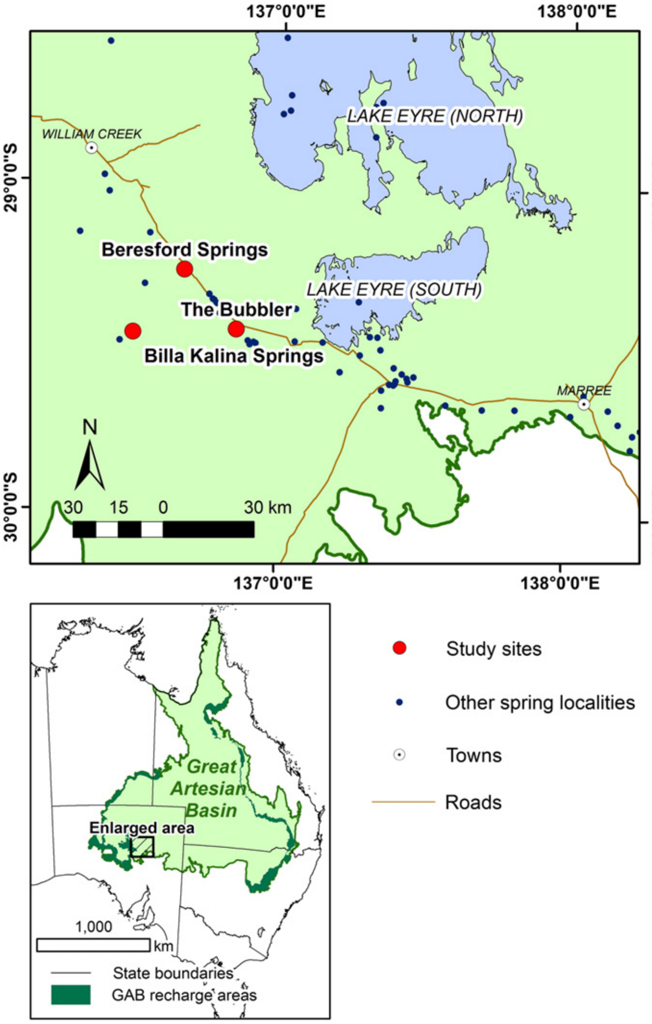

Fig. 1. Location map of the study area, showing the locations of the sampled springs and other mound springs. The location of recharge areas adopted from Radke et al. (2000).