Silicon isotope compositions of euhedral authigenic quartz crystals: Implications for abiotic fractionation at surface temperatures

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ABSTRACT

Silicon (Si) isotopes have been demonstrated as proxies for the paleoenvironmental conditions of various silica deposits. In an effort to investigate the petrogenesis and paleoenvironments of Phanerozoic silica deposits, a suite of euhedral megaquartz crystals in the Cretaceous Edwards Formation from central Texas was petrographically analyzed and their Si isotopic compositions analyzed by bulk and *in situ* techniques. Petrographic analysis shows a close relationship between megaquartz and evaporite minerals. The lithologic association of silica with evaporite-bearing dolomitized carbonate strata suggests that the silicification probably developed in a back-reef tidal-flat environment in which quartz crystals formed after the primary calcite cementation and partial dissolution of evaporites. Silicon isotopic mapping across the megaquartz crystals show that $\delta^{30}Si_{(NBS28)}$ values range from -2.90 to $+2.94$ ‰. These values span the majority of published silicon isotopic values observed in nature and indicate complex growth histories. The negative $\delta^{30}Si$ values are attributed to the dissolution of sponge spicules, which likely act as the primary source of the authigenic megaquartz. The observed range of $\delta^{30}Si$ values in megaquartz crystals is interpreted using a two stage model in which amorphous silica from sponge spicules is dissolved and re-precipitated as megaquartz in a closed system during diagenesis. This Rayleigh-type fractionation model also adds a new level of insight into the abiotic fractionation factor between dissolved and precipitated silica. Based on temperature estimates of 20 to 50 °C for megaquartz precipitation, the fractionation factor was determined to be between -1.8 and -2.1 ‰. The estimated average $\delta^{30}Si$ value of Early Cretaceous seawater is $+2.7$ to $+3.0$ ‰, significantly higher than modern seawater.

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1. Introduction

Silicification in carbonates has occurred throughout the geological record from the Precambrain to Quaternary (Knauth and Epstein 1976; Bustillo 2010). Silica is a common diagenetic constituent in shallow marine carbonate that occurs in a variety of crystal forms and morphologies (Pittman 1959; Folk and Pittman 1971; Chowns and Elkins 1974; Knauth 1979; Milliken 1979; Geeslin and Chafetz 1982; Chafetz and Zhang 1998; Scholle and Ulmer-Scholle 2003). Knauth (1994) classified authigenic silica into 3 types of amorphous opal (opal-A, opal-CT, and opal-C) and 5 types of quartz (granular microcrystalline quartz, megaquartz, length-fast chalcedony, length-slow chalcedony, and zebraic chalcedony). Some of these silica samples have been considered as proxies for paleo-environmental conditions. For example, a number of studies have investigated oxygen isotopic compositions ($\delta^{18}O$) in chert to infer climatic temperatures through time (Degens and Epstein 1962; Knauth and Epstein 1976; Knauth and Lowe 2003), whereas others have attributed zebraic chalcedony to the presence of sulfur in

the water and the association of evaporites (Milliken 1979; Geeslin and Chafetz 1982). However, the mechanism of silicification is not well constrained. Authigenic silica can be formed by: (1) recrystallization of an amorphous silica precursor upon diagenesis (Hesse 1989; Knauth 1994); (2) direct precipitation from aqueous solutions (Mackenzie and Gees 1971; Guidry and Chafetz 2002; Marin et al. 2010); and (3) replacement of preexisting carbonate rocks (Hesse 1989; Knauth 1994). Several possible explanations have been suggested for the replacement of carbonate. These include silica precipitation induced by local decrease in pH that is caused by either biological production of CO_2 (Siever 1962), oxidation of sulfide into sulfate (Clayton 1986; Chafetz and Zhang 1998), or by mixing of marine and meteoric waters (Knauth 1979).

In addition to the uncertainty in the factors controlling precipitation, the sources of silica and their relative contributions are still not well understood. The silica may originate from silica secreting organisms (*e.g.*, diatom frustules, sponge spicules, and radiolarians) or through abiotic processes. Abiotic silica sources in carbonate rocks include volcanic ash, by-products of chemical weathering during clay formations and hydrothermal fluids (Scholle and Ulmer-Scholle 2003). Furthermore, the timing of silicification is not well constrained because examples of early, intermediate, and late silicification have all been described in

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the literature (*e.g.*, Hesse 1989). Bustillo (2010) suggested that the silicification in carbonates during early, shallow burial may occur under quite different conditions than those from later burial stages. Understanding the timing and environmental conditions of silicification along with the sources of silica is crucial in understanding the nature of their diagenesis.

Recent studies (Robert and Chaussidon 2006; Van den Boorn et al. 2010; Chakrabarti et al. 2012; Marin-Carbonne et al. 2012) have used Si isotopes to trace the origin of Archean and Proterozoic chert and the environment of the Precambrian Ocean. Chakrabarti et al. (2012) reported a range of $\delta^{30}Si$ in Precambrian chert samples between -4.29 and $+2.85$ ‰ and suggested a Rayleigh-type kinetic fractionation model to explain the observed range of $\delta^{30}Si$ values. Additionally, it has been demonstrated that $\delta^{30}Si$ can be used to delineate chert that has precipitated directly from seawater compared to hydrothermal chert (Van den Boorn et al. 2007, 2010). Studies of Phanerozoic samples are used to constrain global biogeochemical cycles. Silicon isotope compositions have been measured in a wide range of natural samples that include abiogenic and biogenic (diatom and sponge) silica from marine and fresh waters (Ding et al., 1996; De La Rocha et al. 1997, 2000; De La Rocha 2003; Ding et al. 2005; Fripiat et al. 2007; Georg et al. 2009; Hendry et al. 2010; Ding et al. 2011), soils and silcrete (Basile-Doelsch et al. 2005; Opfergelt et al. 2009; Steinhoefel et al. 2011), as well as silica secreting plants (Ding et al. 2005; Opfergelt et al., 2009). Despite the renewed interest in the application of stable Si isotopes in geologic and biogeochemical problems, there is still a gap between the Precambrian and modern silica samples. Stable Si isotopes of Phanerozoic silica have not been characterized in the literature. Although diatoms, among silica secreting organisms, almost completely control the modern silicon cycle, the dissolved silicic acid concentration and its isotopic composition in the Mesozoic marine waters may be quite different because diatoms did not evolve until the Oligocene (Wells 1983; De La Rocha, 2007). De La Rocha and Bickle (2005) suggested that average values of $\delta^{30}Si$ in marine silicic acid in the "pre-diatom" ocean waters may have been considerably higher than those of the modern ocean.

Experimental studies have been carried out to understand the mechanism and factors that control Si isotope fractionation during precipitation and dissolution (Demarest et al. 2009; Geilert et al. 2014; Oelze et al. 2014; Wetzel et al. 2014). However, the Si isotope fractionation factor between precipitates and dissolved silica in fluids ($\Delta^{30}Si_{prec-diss}$) is still not well constrained. There is a large discrepancy between laboratory experiments and studies of natural samples. Temperature, reaction rate, saturation state, reactive surface area, and flow regime (Li et al. 1995; Delstanche et al. 2009; Geilert et al. 2014) have all been shown to affect the fractionation. For instance, Li et al. (1995) conducted batch experiments on silica precipitation and observed that only under low temperature and very fast precipitation rate will the fractionation factor reach its maximum. Recently, Geilert et al. (2014) used flow-through experiments to produce silica precipitation in the 10 to 60 °C temperature range and observed a negative relationship between the fractionation factor and temperature. A similar temperature dependent trend has also been reported by Roerdink et al. (2015). Basile-Doelsch et al. (2005) used an average $\Delta^{30}Si_{prec-diss}$ value of -1.5 ‰ in their pedogenic and groundwater silcrete studies. Other values of $\Delta^{30}Si_{prec-diss} = -2.3$ ‰ (Van den Boorn et al. 2010), -2.0 and -3.0 ‰ (both in Chakrabarti et al. 2012) have also been used in the literature. It appears that solid-fluid Si isotope fractionation in natural surface condition is poorly constrained and system dependent.

In this study, laser ablation (LA) *in situ* and solution-based bulk Si isotope analyses were applied to doubly terminated authigenic euhedral megaquartz crystals collected from the Cretaceous Edwards Formation at Lake Georgetown Spillway, central Texas. The high spatial-resolution Si isotope data in concert with petrographic and petrologic observations constrain models of the paleoenvironmental conditions during the euhedral authigenic quartz crystal formation. Further, a two-stage Rayleigh-type kinetic model is used to constrain abiotic Si

isotope fractionation factors during quartz formation. Finally, the hypothesis that the "pre-diatom" ocean waters may have higher $\delta^{30}Si$ value than the modern seawater is tested.

2. Geologic background

The Upper Albian Edwards Formation in central Texas is characterized by rudist reefs and associated inter-reef deposits which were formed on an extensive warm shallow marine carbonate platform known as the Comanche Platform (Fisher and Rodda 1969; Mukherjee et al. 2010). The platform was bounded by the deep water Ancestral Gulf of Mexico on the southeast and the shallow marine North Texas — Tyler Basin on the north and west (Fisher and Rodda 1969; Mukherjee et al. 2010). In central Texas, the Edwards is the youngest formation of the Lower Cretaceous Fredericksburg Group, conformably underlain by the Glen Rose Formation and disconformably overlain by the Georgetown Formation (Rose 1972). The surface exposure of the Edwards Formation in central Texas generally parallels the Balcones Fault Zone. On the down-thrown side of the fault zone, the Edwards Formation is found in the subsurface in south-central Texas. Fisher and Rodda (1969) recognized four depositional facies of the Edwards Formation that include: (1) rudist bioherm facies, (2) platform grainstone facies, (3) lagoonal facies, and (4) diagenetic dolomitic facies. Lithologically, the Edwards Formation is composed of both primary and diagenetic limestone, dolomite, chert, and evaporites (Nelson 1973).

The study area is located in the spillway of Lake Georgetown near the city of Georgetown, Williamson County, in central Texas (Fig. 1). The spillway exposes the upper part of the Edwards Formation. The section on the eastern side of the spillway is characterized by a shallowing-upward carbonate sequence that includes subtidal fossiliferous wackestone and thoroughly bioturbated mudstone, intertidal cross-stratified peloidal packstone and grainstone, and supratidal laminated grainstone with displacive evaporite nodules. Euhedral megaquartz crystals are found exclusively in a 15 cm thick horizon within the dolomitic grainstones (Fig. 2). The quartz appears as single euhedral crystals and crystal clusters. Most single crystals are prismatic, either with well-developed double terminations or well-defined crystal faces. Individual crystals range from 1 mm to 1 cm in length. After washing with hydrochloric acid (HCl) to remove carbonate, most quartz crystals appear to be clear with cloudy patches containing fluid and solid inclusions. Crystal clusters are composed of groups of quartz crystals that all developed from a common point of origin. When the quartz grains are viewed in thin sections, the textures and grain morphologies of the quartz found in the Cretaceous Edwards Formation strongly resemble the euhedral megaquartz crystals in Pleistocene sabkha dolomite from the Persian Gulf described by Chafetz and Zhang (1998) and the Herkimer Diamonds (HD, hereafter) in Cambrian Little Falls Dolomite in Herkimer County, New York (Zenger 1976).

3. Analytical methods

3.1. Petrography

Thin sections of dolomitized limestone samples containing megaquartz crystals were studied by both optical and electron-beam techniques. For the electron-beam work, thin sections were carbon coated and imaged with a JEOL JSM 6400 scanning electron microscope (SEM) in backscattered electron (BSE) mode with an accelerating voltage of 15 kV and a working distance of 15 mm. Energy dispersive spectroscopy (EDS) was employed to determine the mineralogy of the inclusions in quartz crystals.

3.2. X-ray diffraction

Carbonate samples that host the quartz were crushed using an agate mortar and pestle. X-ray diffraction (XRD) analyses of host carbonate