[PS]Petrologic and Geochemical Constraints on Authigenic Euhedral Quartz Crystals in Edwards Formation, Central Texas*

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Abstract

Euhedral megaquartz crystals are present in the upper part of Cretaceous Edwards Formation from the spillway of Lake Georgetown, central Texas. The siliceous deposits formed almost exclusively in a 15 cm thick horizon within the carbonate that is underlain by rudist reef buildups. Individual crystals range from about 1 mm to 1 cm in size and many show shallow evaporative anhydrite and calcite crystal inclusions. Proportions of anhydrite inclusions vary considerably between quartz crystals. Most megaquartz crystals are characterized by strongly undulatory extinction. The paragenesis and environmental conditions of silicification are of considerable interest as silicification in carbonates appears to be closely linked to reduction of porosity and permeability. The lithological association of evaporate-bearing dolomitized carbonate strata with rudist reefs suggests that the anhydrite probably developed in a back-reef tidal-flat environment. The occurrence of anhydrite and calcite inclusions implies that precipitation of quartz crystals took place after the primary calcite cementation and partial dissolution of evaporite. Silicification is largely controlled by fluctuation of pH in pore fluids due to the partial dissolution of sulfate during burial and mixing with meteoric water. In situ silicon isotopic analyses on individual quartz crystals are useful in understanding the silicification history. Detailed silicon isotopic mapping across the megaquartz crystals show that d30Si values range from −2.72 ‰ to 2.94 ‰, almost account for the entire silicon isotopic fractionation range in nature, which indicates very complex growth histories. The very negative isotopic signature can be attributed to the dissolution of sponge spicules, which probably act as the primary source of the authigenic megaquartz. The commonly used bulk analysis of dissolving entire grains overlooks the complicated silicon isotopic composition within individual quartz crystals. Thus, combined petrologic and in-situ silicon isotope measurements demonstrate that euhedral authigenic quartz in the Cretaceous Edwards Formation can originate at shallow depth by dissolution and reprecipitation processes.

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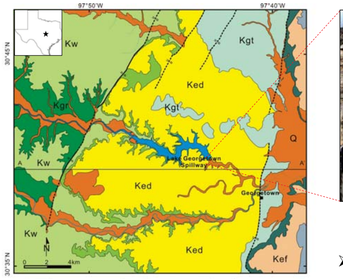
1. Introduction

Doubly terminated euhedral megaquartz crystals occur in the upper part of Cretaceous Edwards Formation at Lake Georgetown Spillway, Central Texas. The siliceous deposits formed almost exclusively in a 15 cm thick horizon within the dolomitized carbonate strata that are underlain by rudist reef buildups. The size of individual crystals range from 1 mm to 1 cm. Lath-shaped evaporative anhydrite inclusions are common in megaquartz

The origin of quartz crystals along with the paragenesis and environmental conditions of silicification are of great interest as silicification in carbonates appears to be closely linked to reduction of porosity and permeability. Petrologic and isotope geochemistry provide great insights in the source, timing and mechanisms of silicification.

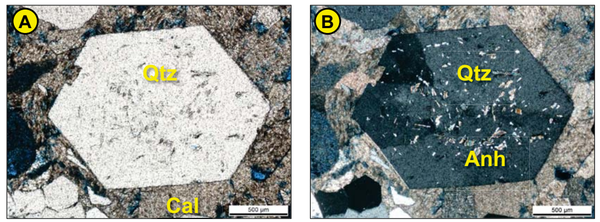
2. Geologic Background



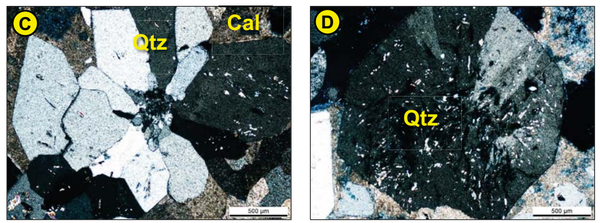
Geologic map of study area (modified from Collins, 2005)

- Central Texas during Early Cretaceous: warm shallow marine carbonate platform with tidal flat environment.
- Edwards Formation: reef complex composed of rudist reefs and inter-reef deposits that grades upward into evaporitic dolomitic tidal flat.

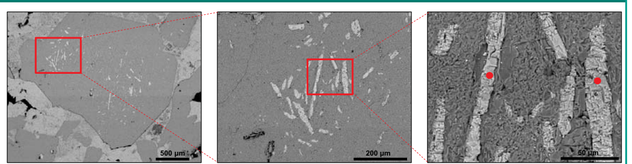
3. Petrography

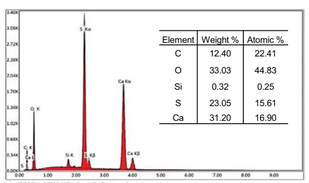


Euhedral megaquartz with quasi-hexagonal crystal habit: (A), plain light; (B), cross polars. Quartz crystals appear to have undulose extinction. (C), Drusy quartz with anhydrite inclusions. Zoned holes in center were probably produced by removal of anhydrite, cross polars; (D), Quartz with nearly fibrous extinction. Patches of elongate vacuoles and anhydrite laths are common.



4. SEM Analyses





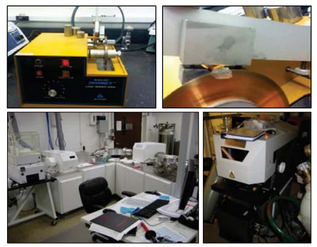
Element	Weight %	Atomic %
C	12.40	22.41
O	33.03	44.83
Si	0.32	0.25
S	23.05	15.61
Ca	31.20	16.90

Backscattered electrons (BSE) images of quartz crystals with anhydrite inclusions as confirmed by energy dispersive X-ray spectrum (EDS) results. The distinctive cleavage perpendicular to the grow axis is also indicative of anhydrite ($CaSO_4$) crystals. No fluid inclusions were found in quartz crystals.

The presence of anhydrite inclusions indicates the precipitation of quartz crystals took place after the precipitation of anhydrite in supratidal flat and before the anhydrite hydrated to gypsum.

5. Silicon Isotopes

Previous studies suggest a local origin for the silica and penecontemporaneous silicification process. Chowns and Elkins (1974) indicated the abundant siliceous sponge spicules in peritidal zones may provide the source for silica. In situ silicon isotope measurements are utilized to give further information on the source of silicification.



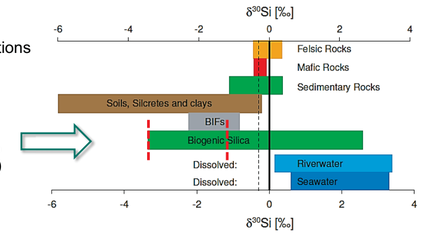
Individual quartz grains are cut along the c-axis using a low speed saw. Silicon isotopic compositions are measured directly on the polished surface of quartz grains using LA-MC-ICP-Ms at University of Houston. Results are reported by δ notation:

$$\delta^{30}Si = \left(\frac{^{30}Si / ^{28}Si_{(sample)}}{^{30}Si / ^{28}Si_{(standard)}} \right) - 1 \times 1000\ ‰$$

The long term precision of $\delta^{30}Si$ is < 0.41‰ (2σ).

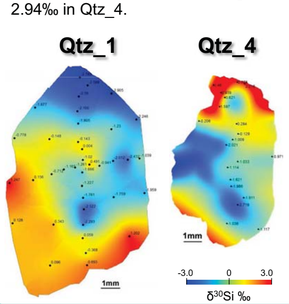
Silicon isotope variations in natural reservoirs (Reynolds ,2011)

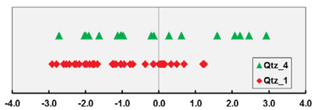
Sponge spicules: $\delta^{30}Si$ = -3.7 to -1.2‰ (De La Rocha, 2003)



6. Results

Results of the silicon isotopic analyses from two megaquartz grains are shown below. The hexagonal crystal habit is well preserved in both grains as exposed in cross sections. $\delta^{30}Si$ values range from -2.91 to 1.25‰ in Qtz_1 and from -2.72 to 2.94‰ in Qtz_4.

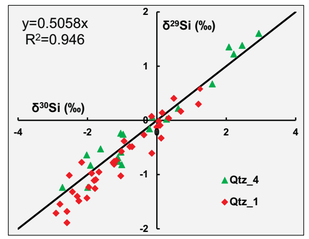




In situ isotopic analyses provide great spatial resolution than traditional bulk measurements. $\delta^{30}Si$ values are plotted at the spots of measurements. Also shown are the interpolated data using Kriging method. The distribution of $\delta^{30}Si$ in a single grain changes systematically. Both samples show relatively depleted cores and enriched rims.

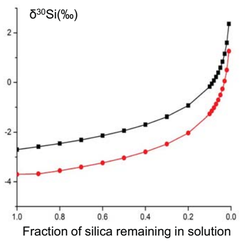
6. Discussion

Petrographic observation and SEM analyses reveal the intimate relationship between silicification and evaporite. Chert nodules, silicified molluscan shells, length-slow chalcedony and megaquartz have been documented in Lower Cretaceous Edwards Formation in Central Texas along the Balcones fault zone just south of the study area (Chowns and Elkins, 1974). The presence of anhydrite and dolomite in the Edwards Formation suggests an arid evaporitive environment similar to sbakhas of the Persian Gulf.



In situ silicon isotopic analyses on individual quartz crystals revealed complicated growth histories. The two analyzed megaquartz grains show similar trend with negative cores and positive rims and the $\delta^{30}Si$ values observed in the cores closely resemble the values of sponge spicules, suggesting the silicification probabry initiated from a ^{30}Si depleted source. Although siliceous silcretes have been documented with $\delta^{30}Si$ value as low as -5.7‰, their contribution in the Edwards formation can be ruled out as no evidence of siliceous silcretes has been found.

- The values of $\delta^{30}Si$ vs $\delta^{29}Si$ follow the mass dependent fractionation line, indicating the fractionation process follow either equilibrium or kinetic fractionation.
- The range and distribution of $\delta^{30}Si$ values observed in quartz samples can be explained by kinetic fractionation model. Simulation of kinetic Rayleigh distillation of silicon isotopes in a closed system is shown on the right. Assume the initial precipitation has $\delta^{30}Si$ = -3.7‰ (sponge spicules). Curves depict changes in the $\delta^{30}Si$ of silica precipitated at each instant (black line) and silica remaining dissolved in solution (red line).
- Alternatively, the large euhedral crystals may form by coalescing smaller nucleus crystals which may have distinctive isotopic signatures. More detailed measurements will be needed.



7. Conclusion

- Petrographic and silicon isotopic data suggest the euhedral megaquartz in Edwards Formation is derived from opaline sponge spicules in an arid evaporitic tidal flat environment.
- Inclusions within megaquartz crystals indicate that silica formed by filling the cavities derived from the dissolution of initial carbonates and anhydrite.
- The lack of fluid inclusions in megaquartz crystals probably indicate that hydrothermal activities during quartz formation can be neglected.
- The $\delta^{30}Si$ in megaquartz almost account for the entire fractionation range in natural reservoirs. The isotopic composition in megaquartz grains can be explained by Rayleigh distillation model.

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