Isotopic compositional characterization of siderite nodules: Implications for the reconstruction of the depositional paleo-environment of the Takoradi Shale Formation, around Essipon, Ghana

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ABSTRACT

The late Devonian to early Carboniferous Takoradi Shale Formation (TSF) of the Sekondian Group outcrops along the western coast of Ghana is typically composed of hard, compact, black or dark grey fissile shale or sandy shale, rich in organic matter. The upper part of the formation is characterized by inclusions of large discoidal nodules of compact, siderite or clay ironstone. The geological history of this formation, however, has not been robustly established. We carried out petrographic and stable isotopic studies on these siderites in order to constrain and understand the depositional environment of the TSF. The results obtained will add to the reconstruction of the geologic history of the formation. A total of 20 samples of the siderite nodules hosted in the shales of the TSF were analyzed for their carbon and oxygen isotope compositions using the laser spectroscopy technique. The $\delta^{18}O$ (VPDB) values of the analyzed samples range from -7.04 to 3.72, whereas $\delta^{13}C$ (VPDB) values typically range from -6.07 to -9.4 per mil. The observed $\delta^{18}O$ values are typical of carbonates precipitated from ^{18}O depleted marine pore waters, suggesting that precipitation of the siderite took place under reducing conditions. The C and O plots place the nodules in the boundary between marine and continental environments, with a larger percentage being marine. The textural fabric of the siderite is marked by separate episodes of calcite veining which reflect the different stages in the diagenetic history of the nodules and the TSF concurrently. The study therefore suggests that the siderite nodules formed during early stages of diagenesis in a marine to near shore environment followed by encroachment of meteoric water. Thus, marine siderite precipitation ceased and calcite became the more stable phase occurring as late forming veins in the siderite nodules, evidenced in the textural fabrics.

Keywords: siderite, stable isotope, geochemistry, depositional environment, Takoradi Shale Formation, Sekondian Group.

Introducton

The Takoradi Shale Formation (TSF) is one of the formations of the Ordovician to early Cretaceous sedimentary rocks of the Sekondian Group. It is well exposed along the coasts of the Western and Central regions of Ghana (Figure 1). These formations have over the years been studied by many researchers (e.g. Atta-Peters and Annan-Yorke, 2003; Asiedu *et al.,* 2005; Asiedu *et al.,* 2010), resulting in diverse ideas and conclusions about its depositional history. Previous studies on the TSF have utilized micropaleontological and bulk rock geochemical data of the shale to infer its depositional environment and paleoclimate (Atta-Peters *et al., 2003,* Asiedu *et al., 2010*). These studies suggest a marginal marine depositional environment for the formation. Recent sedimentological studies on the TSF, however, suggest that deposition took place in a deltaic environment (Agbetsoamedo, 2014).

Geochemical parameters have been used by various authors to understand the paleo-oxygenation and depositional conditions of ancient sediments (e.g. Jones and Manning, 1994). Noteworthy amongst these geochemical parameters are the stable isotope compositions of siderite and pyrite mineralization in sediments and sedimentary rocks. Reducing environments tend to favor siderite precipitation (Berner, 1971), thus it is a useful indicator of oxidation-reduction conditions in sediments. Furthermore, it is reasonable to assume that siderite, as a common early diagenetic mineral, is more likely to be influenced by the chemistry of the depositional setting than later minerals that form from more evolved pore waters. Hence, Mozley (1989) demonstrated a strong relation between the geochemistry (including isotopic composition) of early diagenetic siderite and depositional environment. Because siderite is often one of the earliest minerals to precipitate in sediments, there has been considerable interest over the years in using its geochemistry as an indicator of its depositional environment.

The isotopic data should reflect the diagenetic environment of mineral precipitation and this can be based on the present day understanding of the formation of siderite. In places where petrographic evidence indicates early siderite formation, the geochemical data may be used to determine the environment of sediment deposition (i.e. whether it is marine, brackish or fresh water).

In this study, the depositional environment of the TSF has been inferred from the carbon and oxygen isotopic compositions of the siderite nodules present in the shale part of the TSF. The stable isotopic ($\delta^{13}C$ and $\delta^{18}O$) compositions of the diagenetic minerals, siderite and pyrite, which are common mineral constituents in the TSF, have also been used to interpret the evolution of the pore water within the sediments.

Geology of the Study Area

On the basis of lithology and stratigraphy, Mensah (1973) proposed seven formations for the Sekondian Group. This Group is about 1200m thick and consists of a predominantly fine-grained basal unit, Ajua Shale, overlain by six predominantly arenaceous lithologic units (Figure 2). The rock types vary in proportions within each formation, but in all sandstones dominate (about 55%), followed by shale/siltstone (40%) and conglomerate (5%). The Sekondian Group rests unconformably on the Paleoproterozoic Birimian Supergroup. The rocks are extensively faulted but unmetamorphosed (Mensah, 1973).

The Takoradi Shale Formation is sometimes classified with the underlying sandstone formation as Takoradi Beds. The Formation is about 200 m thick and it is typically composed of hard, compact, black or dark gray fissile shale or sandy shale, rich in organic matter. The base of the Takoradi Shale Formation is composed of thin bedded micaceous sandstones which intercalate with grey shales. The upper part of the succession shows interbedded grey-green grit bands and nodules of fine, grey lenticular sandstones up to several meters thick. Also included are siderite nodules and gypsum which occurs as thin veins traversing the shale and trends parallel to the bedding planes (Atta-Peters *et al.,* 2003).

Siderite Occurrence in the Field

Along the coast of Essipon, the TSF is characterized by large discoidal nodules of compact, finely granular siderite or clay ironstone. The nodules range in diameter from 10cm to 40cm and occur along the bedding planes in the fissile carbonaceous shale portions of the formation (Figure 3). Oxidation of the iron content in the nodules results in reddish colorations on the surfaces of the nodules. Pyrite also occurs as microscopic disseminations in the upper parts of the exposures. Paleontological studies have shown that the TSF are characterized by terrestrial miospores and marine acritarchs. Interpretations based on these microfossils have indicated Late Devonian/Early Carboniferous age for the formation which is deposited in a near shore-coastal (deltaic) environment (Atta-Peters *et al.,* 2003).

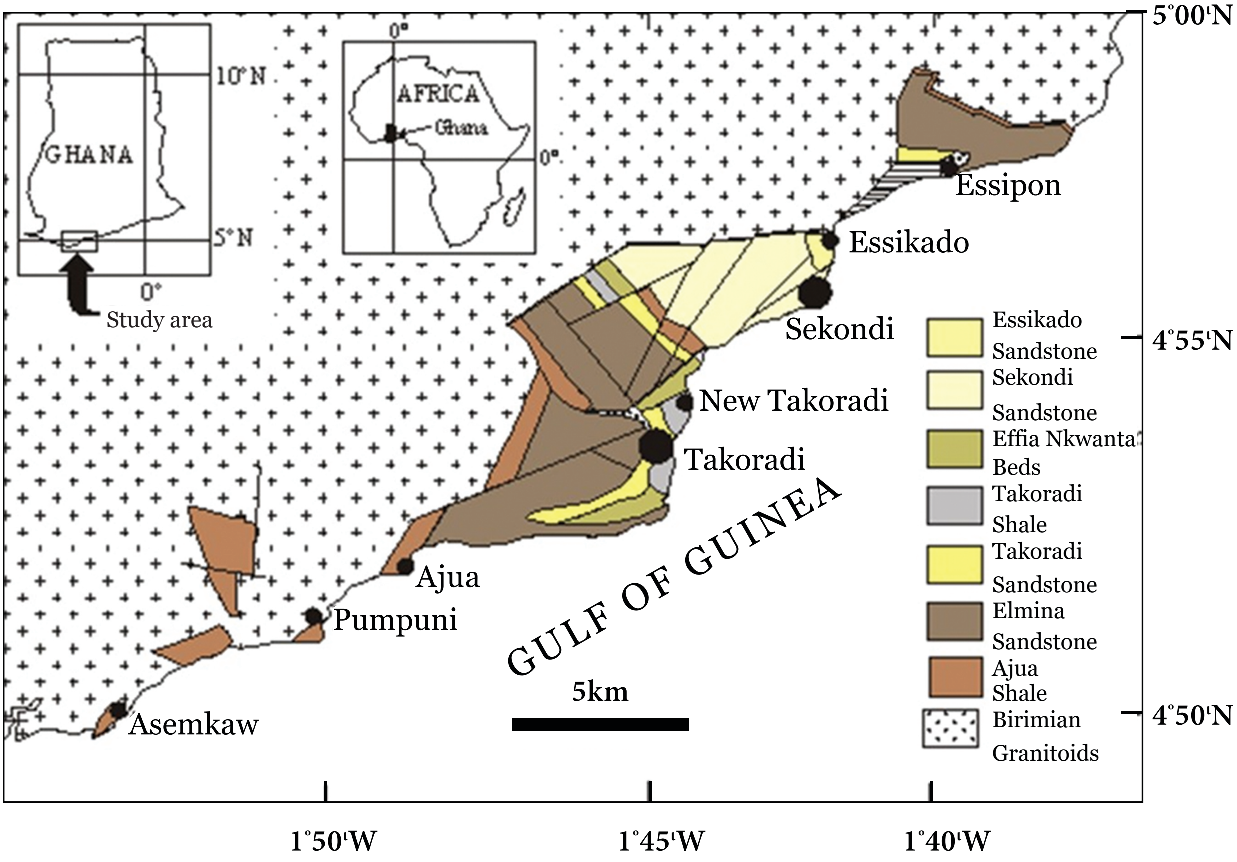


Fig. 1: The simplified geological map of the Sekondian Group in the Sekondi–Takoradi area, Ghana (after Asiedu *et al., 2005*; inset showing the map of Ghana and Africa).

Methods

A total of 30 samples of the siderite nodules were collected from the TSF outcrops along the Essipon beach, Takoradi. Twenty (20) of these were prepared (cleaned and cut) at the laboratory of the Department of Earth Science, University of Ghana. Samples were collected for isotopic measurement and analysis in a commercial laboratory (ALS minerals, Canada). Laser Spectroscopy was adopted in the analysis for the C and O isotopic composition of the siderite nodules. A prepared sample (0.035g) of the siderite nodule was reacted with concentrated phosphoric acid at 72°C for 1 hour. The CO_2 gas produced was then measured for carbon and oxygen isotopes by off-axis integrated cavity output laser spectroscopy. Results for $\delta^{13}C$ were calculated relative to Vienna Pee Dee Belemnite (VPDB) and results for $\delta^{18}O$ were calculated relative to Vienna Standard Mean Ocean Water (VSMOW). Analytical errors were 0.3‰ for $\delta^{13}C$ and 0.5‰ for $\delta^{18}O$. Fractionation factors were used for calcite ($CaCO_3$) where necessary. A total of 30 samples, 20 samples of the siderite nodules and 10 samples of the siderite lenses/bands) were prepared for petrographic analysis aimed at determining their mineralogical composition. This was carried out in the laboratory of the Department of Earth Science in University of Ghana, Legon. Mineral identification and modal percentages of minerals under thin section were estimated by the use of the petrographic microscope and visual estimation charts. Photomicrographs were then taken for each thin section examined. All petrographic observations made were employed for determining or inferring the diagenetic history of the siderite nodules.

Results

Siderite petrography and Stable Isotope Composition

Thin section analysis revealed that the siderite nodules contained about 90-99% siderite oolitic grains with minor occurrences of late diagenetic calcite veins, rhodochrosite disseminations and silica grains. The veins vary in size from about 0.1mm to 2mm (Figure 4). The mode of formation of siderites is often characterized by peculiar textural variations. The siderite nodules in the TSF occur as an assemblage of well-sorted, silt-sized grains (up to 0.1 mm) in about 90% of the sample slides, to zones of predominantly sideritic nodules, lenses and bands up to 5 cm thick. The concentration of the siderite in the nodules ranges from sediments with about 60 volume percent (in a few instances) and can reach 95 volume percent of the nodule (in many instances). The samples that showed less than 60% siderite composition were typical of the lenses and bands occurring in the TSF.

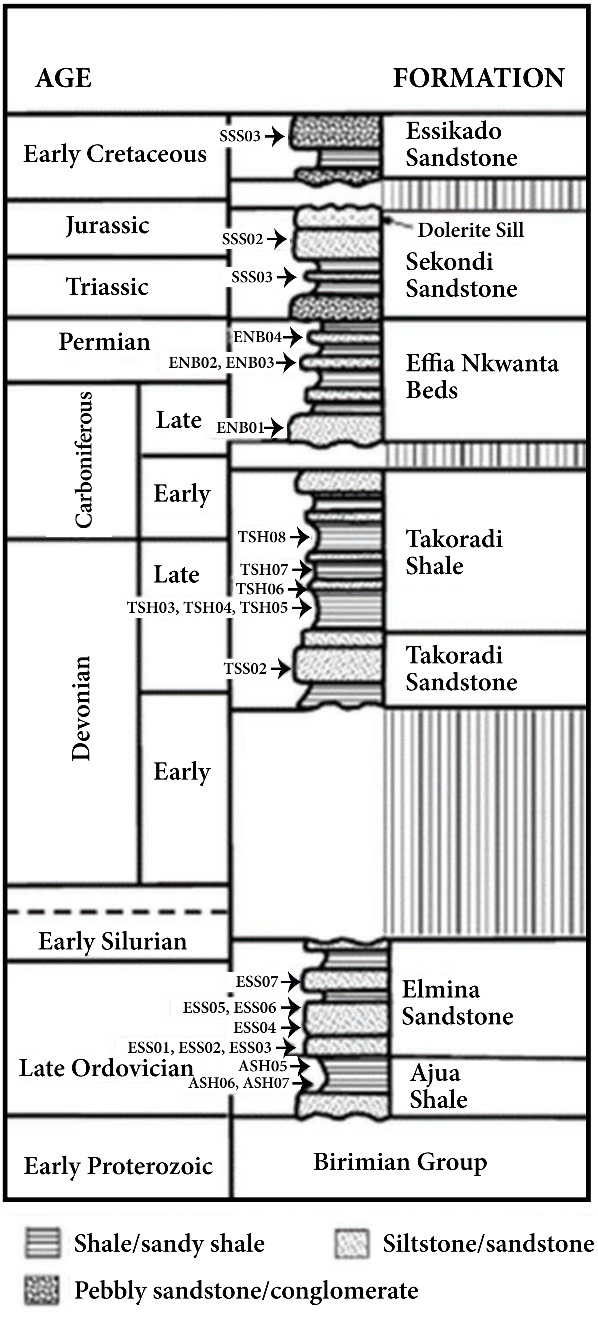
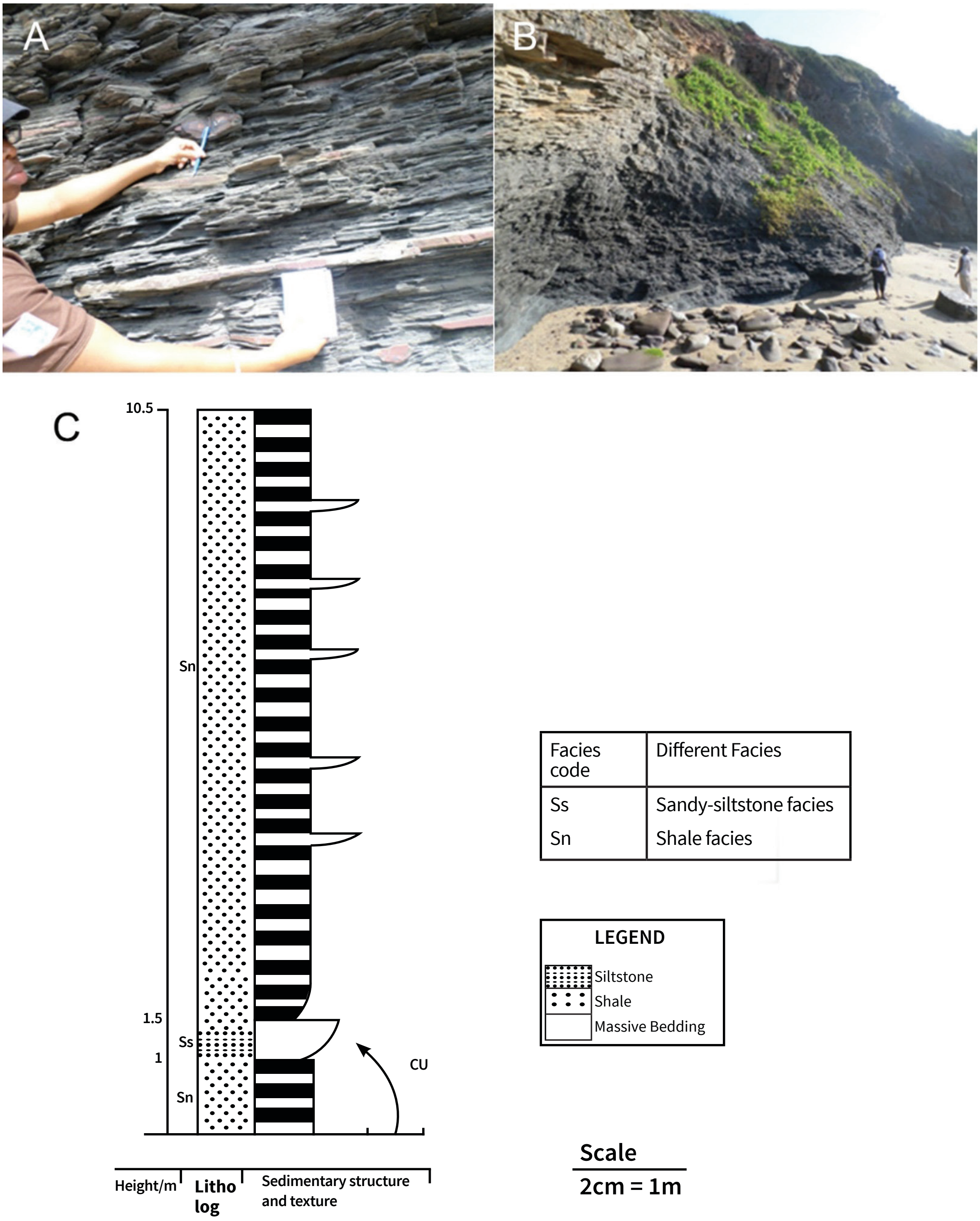


Fig. 2: Stratigraphic column of the Sekondian Group (after Asiedu *et al., 2005*)



Facies code	Different Facies
Ss	Sandy-siltstone facies
Sn	Shale facies

Fig. 3: (A) Siderite nodules embedded in the dark grey carbonaceous shale of the TSF (B) Vertical section of the TSF showing the dark grey, siderite nodule-bearing carbonaceous shale (C) Lithostratigraphic log of the dark grey carbonaceous section of the TSF.

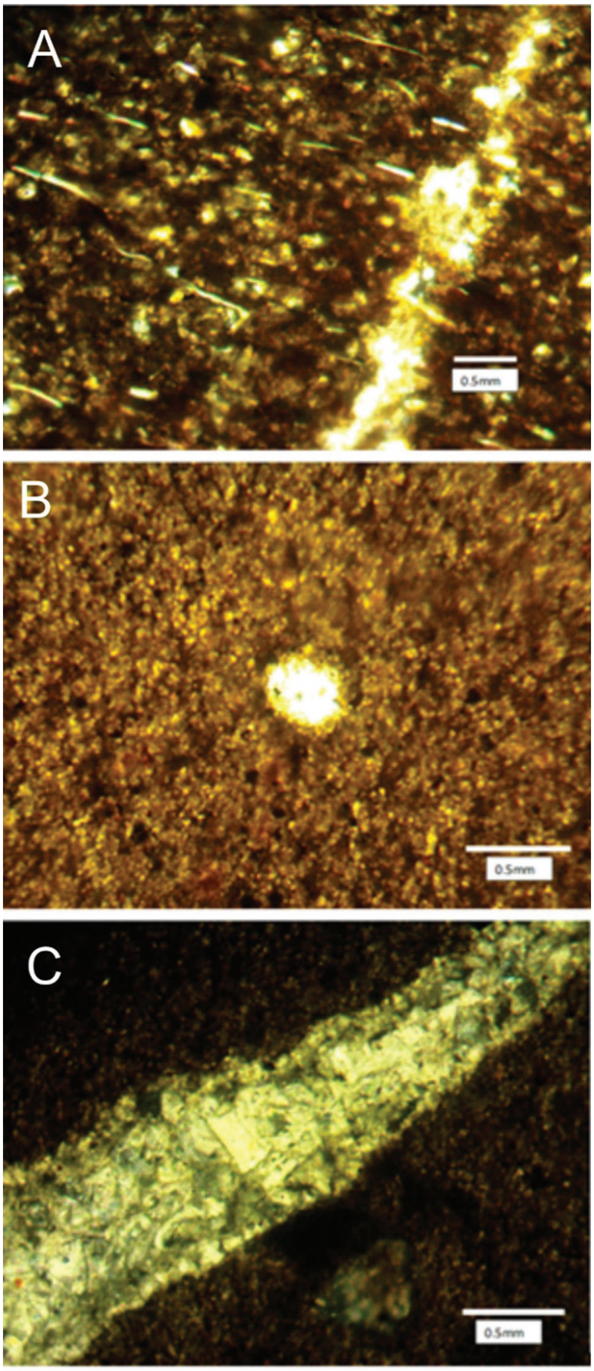


Fig. 4: Photomicrograph of siderite showing A) Silica and Rhodochrosite dissemination in siderite B) Fine grained oolitic siderite, about 98% composition C) About 1mm thick calcite vein.

The $\delta^{18}O$ values range from 23.6 to 34.7 per mil (VSMOW) or -7.04 to 3.72 (VPDB) while those of the $\delta^{13}C$ range from -6.07 to -9.4 per mil (VPDB) with two exceptions of -14.75 and -11.9 per mil (Table 1).

Table 1. Carbon and oxygen isotopic compositions of siderite nodules from the TSF

SAMPLE DESCRIPTION	Delta ^{18}O (VSMOW) Per mil	Delta ^{13}C (VPDB) Per mil	Delta ^{18}O (VPDB) Per mil
SN001	27	-8.87	-3.75
SN002	28.3	-6.07	-2.48
SN003	30.1	-6.26	-0.74
SN004	27.2	-8.52	-3.55
SN005	32.5	-14.75	1.58
SN006	30.4	-7.44	-0.45
SN007	34.7	-9.4	3.72
SN008	30	-8.72	-0.83
SN009	27.5	-8.18	-3.26
SN010	25.9	-7.39	-4.81
SN011	24.7	-5.01	-5.97
SN012	26.6	-8.79	-4.13
SN013	25.4	-8.09	-5.30
SN014	24.2	-6.75	-6.46
SN015			-29.94
SN016	26.5	-7.26	-4.23
SN017	29.8	-11.9	-1.03
SN018	26.8	-8.64	-3.94
SN019	23.6	-8.17	-7.04
SN020	24.8	-6.99	-5.88

Pee Dee Belemnite (PDB) = 0.970065smow - 29-94 (Friedman and O'Neil, 1977).

Discussion

Petrography

The siderite can be said to be authigenic or diagenetic, which suggests precipitation from no calcite precursor, (Baker, 1996; Chamley, 1989), considering their compositional make up and field relations with respect to the host rock (where they tend to form within the beds/laminae). The TSF is carbonaceous and thus rich in organic matter, hence the bacterial reduction of organic matter in the sediment most likely produced the required carbonate for siderite precipitation. Bacterial reduction of organic matter, which often takes place during shallow burial, generates water, carbon dioxide, and biogenic methane. This increases the pH of the pore fluids, creating a more alkaline fluid which can lead to precipitation of carbonates. Carbonate precipitation of this kind often occurs patchily as concretions which develop intermittently along bedding surfaces. In addition, the iron (high Fe/Ca ratio) necessary to produce the siderite could have been adsorbed on pelagic clays in the sediments (Basov *et al.,* 1979; Matsumoto, 1989). The siderite nodules are also characterized by calcite ($CaCO_3$) veins, rhodochrosite ($MnCO_3$) disseminations and some silica (SiO_2). These are late stage diagenetic minerals which formed after the precipitation of the siderites. Pyrite is another mineral observed in the TSF which indicates that the sediments have passed through a stage of sulphate reduction.

Carbon and Oxygen Compositions

The carbon and oxygen isotopic compositions (Table 1) of the TSF siderite nodules were plotted on a discriminatory diagram to help determine the possible environment of deposition. The ^{13}C and ^{16}O values for the siderite nodules show depleted values with somewhat minimal variations that plot closely to the marginal marine environment (Figure 5). The small variation in $\delta^{13}C$ values is attributable to the less extensive bacterially facilitated reactions. These reactions involve the decomposition of organic matter which is known to control pore water $\delta^{13}C$ compositions in organic rich sediments. The negative carbon values for the diagenetic siderite can be said to be produced during ferric iron reduction (suboxic conditions) and during or immediately after sulfate reduction in a marginal marine environment (which has a mixture of marine and non-marine pore waters) as suggested by some earlier researchers (Atta-Peters and Annan-Yorke, 2003). The oxidation of methane near the base of the zone of sulfate reduction could also contribute to the negative carbon values (Raiswell and Berner, 1987). The negative values also rule out any possibility that the carbon content of the TSF siderite nodules could have been formed from the input of ^{13}C-enriched bicarbonate derived from methanogens, ^{13}C-enriched volcanic gas entering the water body, bicarbonate from dissolution of biogenic ^{13}C-enriched calcite, or the high productivity of ^{12}C-enriched planktonic algae, which would have resulted in ^{13}C enrichment of the residual carbon pool (Fritz *et. al.,* 1971).

The $\delta^{18}O$ values for the siderite nodules are generally negative (depleted) and show minimal variation. The depleted oxygen values are characteristic of marginal marine originated pore water, and the possible explanations for this depletion are recrystallization, precipitation at anomalously high temperatures, water-sediment interaction, mixing with meteoric water and variation in seawater composition. The most likely explanation for this instance would be either mixing of meteoric water and marine waters in marine shelf sediments or mineral water interaction during early diagenesis (i.e. precipitation of ^{18}O enriched minerals in the nodules or host rock which would cause a net depletion of $\delta^{18}O$ in the pore water). However, the latter can be ruled out of the possible cause, considering the fact that the minerals in the TSF (host rock) are ^{18}O depleted, and thus should rather have made the siderite nodules ^{18}O enriched.

The depleted oxygen values of the TSF siderite nodules also place them in an anoxic or euxinic environment. Euxinic environments are those in which the circulation of water is restricted, leading to highly depleted oxygen levels or anaerobic conditions in the water.

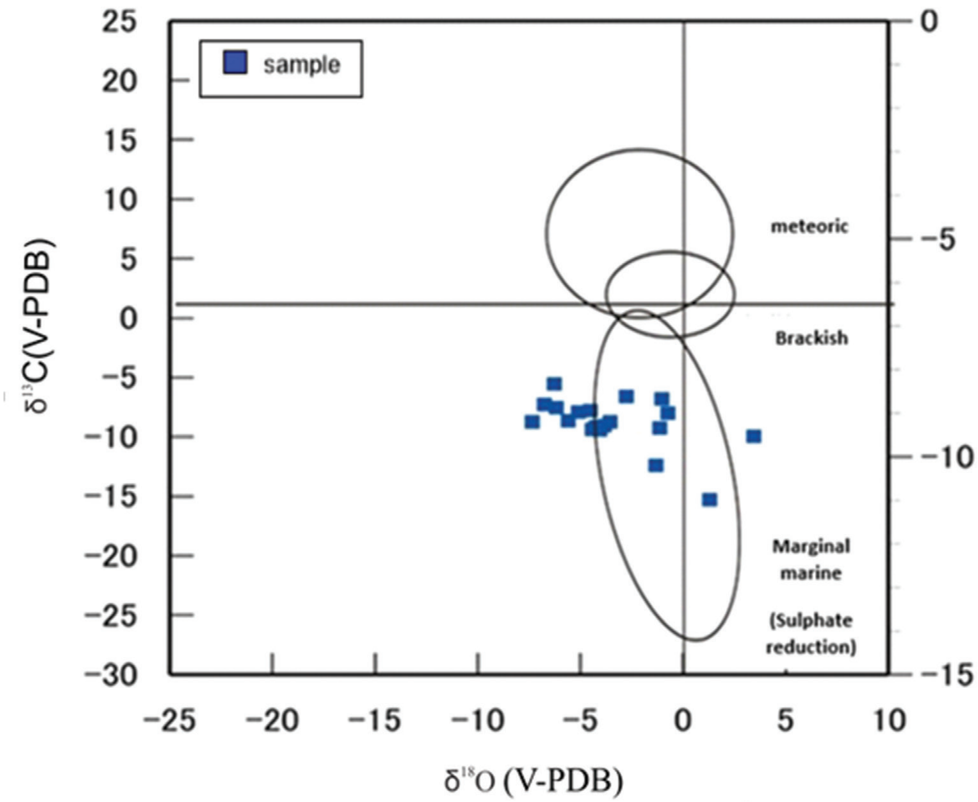


Fig. 5: Plot of δ^{13}C against δ^{18}O values for siderite nodules from the TSF, modified after Mozley and Wersin (1992).

Euxinic also implies anoxic conditions with the presence of excess sulphur that binds with hydrogen to form hydrogen sulfide (H_2S), and this is evidenced in the siderite nodules and the TSF. Such conditions may also develop in swamps, barred basins, stratified lakes, and fiords. Euxinic sediments are those deposited in such conditions, and are usually black and organic-rich.

Both the oxygen and carbon isotopic compositions of the siderites in the TSF were used in predicting the environments of deposition of the TSF. Zymela (1996) used assumptions to conclude that at relatively normal temperatures (typical of tropical climates today) the $\boldsymbol{\delta}^{18}$O values of early precipitated carbonate would be near 0 to -2 $^{o}/_{oo}$ (PDB). Mineral precipitation in freshwaters would result in more negative values due to the lighter isotopic composition of meteoric water. In brackish water, which represents mixed waters of the two environments mentioned above, early formed carbonates should display transitional values between the two end members (Baker, 1996). Late stage marine siderites which formed at greater depths may exhibit more negative δ^{18}O values. This is a reflection of increasing temperatures with depth of burial. Therefore, zoned concretions which formed over a wide depth range should reveal increasingly lighter δ^{18}O from the core to the edge (assuming that the system remained more or less closed). Such decreasing oxygen isotope trends in various concretions have been observed by several authors (Timofeyeva *et al., 1976*; Irwin, 1980; Hennessy and Knauth, 1985; Mozley and Carothers, 1992).

A compilation of both C and O isotopic compositions plot the siderite nodules in the transition between marine and continental environments (near shore to brackish environments). However, a larger percentage of the samples exhibit higher marine signatures than continental when compared to the plots of continental and marine isotopes by Mozley and Wersin (1992). They showed that marine and non-marine siderites are characterized by distinctive compositional trends. Marine siderites generally plot in a field ranging from very low $\delta^{13}C$ values and relatively high $\delta^{18}O$ values to relatively high $\delta^{13}C$ values and low $\delta^{18}O$ values. Non-marine siderites generally have higher $\delta^{13}C$ values than marine siderites. This feature is evident in the samples of the siderite nodules as well. They show low ^{13}C values and very low ^{18}O values, and this thus places the siderite nodule samples in a marginal marine environment, evidenced by the plots.

Conclusion

Results from the isotopic analysis of siderite nodules in the Takoradi shale formation (TSF) suggests a mixture of terrestrial and marine pore fluids which resulted in the precipitation of the siderites. The oxygen and carbon isotopic data for siderites from the TSF showed minimal variation in compositional fields. The $\delta^{18}O$ values range from 23.6 to 34.7 per mil (VSMOW) or -7.04 to 3.72 (VPDB) while those of the $\delta^{13}C$ range from -6.07 to -9.4 per mil (VPDB) with two exceptions of -14.75 and -11.9 per mil. The siderites have $\delta^{18}O$ values characteristic of carbonates precipitated from ^{18}O depleted marine pore waters. The depleted isotopic values plot the siderite nodules in the marginal marine environment. It can also be concluded that the siderites formed during the early stages of diagenesis in a subaqueous environment, which is evident in the mineralogical and textural features of the siderite nodules. The high siderite composition (60-90%), with very minimal late stage occurrences of calcite veins and silica disseminations, suggests very minimal alteration of iron bearing minerals in an environment with reducing conditions. It is suggested that the TSF was deposited in a marginal marine (to brackish) environment, under early diagenetic processes.

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References

Agbetsoamedo, J. E. (2014). Depositional environment of the Takoradi Shale Formation, south western Ghana. (Unpublished Master’s thesis). University of Ghana, Accra, Ghana.

Asiedu, D. K., Hegner, E., Rocholl, A. & Atta-Peters, D. (2005). Provenance of Late Ordovician to Early Cretaceous sedimentary rocks from southern Ghana, as inferred from Nd isotopes and trace elements. *Journal of African Earth Sciences*, 41, 316–328.

Asiedu, D. K., Atta-Peters, D., Hegner, E., Rocholl, A & Shibata, T. (2010). Palaeoclimatic control on the composition of Palaeozoic shales from southern Ghana, West Africa. *Ghana Mining Journal*, 12, 7–16.

Atta-Peters, D. (2000). Early Cretaceous miospores from the Essikado Sandstone Formation of the Sekondian Group of Ghana. *Revista Espanola de Micropaleontologia*, 32, 245–257.

Atta-Peters, D. & Anan-Yorke, R. (2003). Latest Devonian and Early Carboniferous pteridophytic spores from the Sekondi Group of Ghana. *Revista Espanola de Micropaleontologia*, 35, 9-27.

Baker, J. C., Kassan, J. & Hamilton, E. J. (1996). Early diagenetic siderite as an indicator of depositional environment in the Triassic Rewan Group, southern Bowen Basin, eastern Australia. *Sedimentology*, 43, 77-88.

Basov, V. A., Lopatin, B. G., Gramberg, I. S., Danjushevskaya, A. I., Kaban’kov, V. Y., Lazurkin, V. M. & Patrunov, D. K. (1979). Lower Cretaceous lithostratigraphy near Galicia Bank. *Initial Reports of the Deep Sea Drilling Project*, 47, 683-717.

Berner, R. A. (1971). *Principles of sedimentology*. New York: McGraw-Hill.

Chamley, H. (1989). *Clay Sedimentology*. Berlin: Springer.

Claypool, G. E., Holser, W. T., Kaplan, I. R., Sakai, H. & Zak, I. (1980). The age curves of sulphur and oxygen isotopes in marine sulphate and their mutual interpretation. *Chemical Geology*, 28, 199-260.

Friedman, I., & O'Neil, J. R. (1977). *Data of geochemistry: Compilation of stable isotope fractionation factors of geochemical interest* (Vol. 440). Washington, D.C.: US Government Printing Office.

Fritz, P., Binda, P.L., Folinsbee, F.E., & Krouse, KR. (1971). Isotopic composition of diagenetic siderites from Cretaceous sediments in Western Canada. *Journal of Sedimentary Petrology*, 41, 282-288.

Hennessy, J., & Knauth, L. P. (1985). Isotope variations in dolomite concretions from the Monterey Formation, California. *Journal of Sedimentary Petrology*, 55, 120- 130.

Irwin, H. (1980). Early diagenetic carbonate precipitation and pore fluid migration in the Kimmeridge Clay of Dorset, England. *Sedimentology*, 27, 577-591.

Jones, B., & Manning, D. A. (1994). Comparison of geochemical indices used for the interpretation of palaeoredox conditions in ancient mudstones. *Chemical Geology*, 111, 111-129.

Matsumoto, R. (1989). Isotopically heavy oxygen-containing siderite derived from the decomposition of methane hydrate. *Geology*, 17(8), 707-710.

Mensah, M. (1973). On the question of the age of the Sekondi Series, Upper Devonian or Lower Carboniferous rocks of Ghana. *Ghana Journal of Science*, 13, 134–139.

Mozley, P. S. (1989). Relation between depositional environment and the elemental composition of early diagenetic siderite. *Geology*, 17, 704-706.

Mozley, P. S., & Carothers, W. W. (1992). Elemental and isotopic composition of siderite in the Kuparuk Formation, Alaska: Effect of microbial activity and water/sediment interaction on early pore-water chemistry. *Journal of Sedimentary Research*, 62, 681-692.

Mozley, P. S., & Wersin, P. (1992). Isotopic composition of siderite as an indicator of depositional environment. *Geology*, 20, 817-820.

Raiswell, R., & Berner, R. A. (1987). Organic carbon losses during burial and thermal maturation of normal marine shales. *Geology*, 15, 853-856.

Timofeyeva, Z.V., Kuznetsova, L.D. & Dontsova, Y.I. (1976). Oxygen isotopes and siderite formation. *Geochemistry International*, 13, 101-112.

Zymela, S. (1996). Carbon, oxygen and strontium isotopic composition of diagenetic calcite and siderite from the Upper Cretaceous Cardium formation of western Alberta. (Unpublished doctoral dissertation). McMaster University, Ontario, Canada.