

Research Article

Pre-Eruptive CO₂-Rich Fluid Interactions and Siderite Genesis at the Monoun Maar Volcano, Cameroon Volcanic Line: Insights from Stable Carbon and Oxygen Systematic

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Abstract

The Monoun Maar Volcano (MMV) is a polygenetic small-volume volcano within the Cameroon Volcanic Line (CVL), characterized by volcanic eruptions and CO₂-rich fluid interactions. Among its deposit sequence, a pyroclastic deposit unit is identified containing encrustations of ferrous carbonates, whose associated iron and genetic links remain poorly constrained. This study integrates petrographic, stable $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ isotopes, and palaeosalinity-paleotemperature modelling to elucidate the origin of siderite within this pyroclastic ejecta. Siderite occurs as pale yellow-brown massive aggregates within or at the border of some clasts, associated with pyroxene, plagioclase, and olivine. Isotopic data show $\delta^{13}\text{C}_{\text{VPDB}}$ values ranging from -6.0 to -5.2‰, consistent with a magmatic CO₂ source or the oxidative degradation of organic matter. $\delta^{18}\text{O}_{\text{VSMOW}}$ values are relatively high, around 31.4 to 32.3‰, suggesting a freshwater depositional environment influenced by meteoric water and magmatic CO₂. These isotopic values are also consistent with an authigenic carbonate formation likely affected by CO₂ emissions from submerged volcanic chimneys, although an allogenic origin might also be considered. Calculated palaeosalinity ($Z = 115.2$ to 117.34‰) is quite high, indicating saline hydrothermal fluids. Calculated paleotemperatures ($T = 247.93$ to 248.03 °C) are consistent with hydrothermal systems or magmatic-hydrothermal interactions. The calculated palaeosalinity and paleotemperatures support the involvement of high-temperature, CO₂-rich fluids interacting with sediments and tephra from earlier eruptive phases at the bottom of the MMV crater. These findings contribute to a better understanding of the polygenetic eruptive evolution of the Monoun maar and highlight the role of carbonate mineralization in such volcanic settings.

Keywords

Cameroon Volcanic Line, Monoun Maar Volcano, Siderite, Stable Isotopes, Palaeosalinity, Palaeotemperature

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1. Introduction

Maar volcanoes form from phreatomagmatic eruptions when rising magma interacts explosively with groundwater, intersecting the country rocks to create a shallow or deep crater depending on the depth of the explosion locus [29-31, 52, 53]. Additionally, during the progression of the eruption, magma and water fluxes may undergo waning or waxing stages, leading to variations in eruptive styles, including strombolian and/or effusive activities [2, 16, 33, 37, 47, 48].

Monoun Maar Volcano (MMV), located within the Cameroon Volcanic Line (CVL), is primarily known for its lake, Lake Monoun, which garnered global attention following a limnic CO₂ eruption in 1984 that resulted in 37 fatalities, underscoring the importance of ongoing geological investigations. Despite this necessity, it was only recently that the first description of the eruptive evolution of the volcano was proposed [37]. Through comprehensive volcanostratigraphy, geochemical constraints, and geochronological dating, these authors determined that the MMV is a complex polygenetic maar comprising five stratigraphic units from three WSW-ENE aligned craters.

Previous studies following the limnic eruption focused primarily on the lake's geochemistry, bathymetry, and gas emissions [13, 19, 20, 24-27, 42, 45]. Among these works, it was revealed that the deep-water sediments of the lake contain a significant amount of siderites (FeCO₃) and are also saturated with magmatic CO₂ inputs from submerged vents [26, 32, 42, 45]. For instance, Sigurdson et al. [42] attributed the high Fe²⁺ levels that formed the iron siderites in these sediments to the reduction of laterite-derived ferric hydroxides, implying an allogenic origin, meaning that these carbonates were transported from elsewhere, potentially carrying isotopic signatures from the surrounding environments.

However, carbonates can have an authigenic origin, indicating that they might form in place during sedimentation, often influenced by local geochemical conditions, especially under an influx of carbonate-rich fluids. The presence of siderite in crater lake sediments, particularly those influenced by deep magmatic fluid circulation, points to a distinct and fascinating origin story. Unlike siderites in typical lacustrine environments, which primarily derive their components from weathering and oxidative degradation of organic matter within the lake's catchment, siderites found in crater lakes are often intimately linked to hydrothermal activity and volcanic degassing. In such settings, deep magmatic fluids ascend towards the surface, carrying a significant payload of dissolved minerals and gases. The key contributions of these fluids to siderite formation include:

1. Elevated Carbon Dioxide (CO₂) Supply: Magmatic degassing releases significant CO₂ into the crater lake, dissolving in the water to form carbonic acid, which dissociates into bicarbonate (HCO₃⁻) and carbonate (CO₃²⁻) ions, the essential components for carbonate

minerals like siderite. This carbon source often gives siderite a distinct isotopic signature, differentiating it from those formed from organic or atmospheric carbon.

2. Iron (Fe) Source: Hydrothermal fluids are often enriched in dissolved iron (typically as Fe²⁺) leached from the surrounding volcanic rocks or directly exsolved from magma. These fluids can directly vent into the lake bottom or interact with existing sediments, increasing the local concentration of dissolved iron.
3. Creation of favourable geochemical conditions:
 - 1) Anoxia: Volcanic crater lakes can become stratified, with deeper anoxic (oxygen-poor) waters. This condition is crucial because it allows dissolved ferrous iron (Fe²⁺) to remain in solution and be available for siderite precipitation. If oxygen were present, iron would rapidly oxidize to ferric iron (Fe³⁺) and precipitate as iron oxides/hydroxides.
 - 2) pH Modulation: The influx of acidic volcanic gases (like SO₂, HCl) can initially lower pH, but subsequent water-rock interactions and the buffering capacity of the system, along with CO₂ dissolution, can create localized zones with pH conditions suitable for carbonate precipitation.
 - 3) Temperature: While not always a primary driver for precipitation, hydrothermal inputs can influence bottom water temperatures, potentially affecting reaction kinetics.

Although Lake Monoun might fulfil the precedent conditions favourable for an authigenic development of the siderites found there, this aspect has never been explored, nor their genetic links to the eruptive processes. According to Stix and de Moor [43], long-term influx of carbonate-rich fluids under a sealed volcanic system can lead to hydrothermal eruptions fuelled by overpressurization of magmatic gases. Such hydrothermal eruptions might also occur when magmatic gases supply a nearby hydrothermal system through open-vent degassing, vaporizing liquid water, and causing these eruptions.

The pioneer study by Nche et al. [37] identified five stratigraphic units in the MMV: a surge unit on a thick paleosol, weathered scoria fall, and lava flow in the NW crater rim. In the SE part, these units are overlain by a scoria fall and a voluminous surge unit, covered by a second paleosol. Two additional units of about 19 m and 2 m thick respectively separates the deposits recognized as units C and D in the SE rim. These units consist of alternating layers of lapilli ash, tuff, coarse tuff breccia, and lapilli at the base, with carbonate precipitates encrusting most clasts, and medium tuff breccia at the top with the absence of carbonate precipitates.

The present study focuses on this particular siderite-rich unit to investigate the authigenic origin of these siderites and their importance to the eruptive history of the MMV. Using stable isotopic composition (δ¹³C, δ¹⁸O) combined with pe-

trography analysis, and paleoenvironmental modelling, we (1) determine the sources of carbon and oxygen in siderite, (2) reconstruct the paleoenvironmental conditions during carbonate precipitation, and (3) propose a genetic model for siderite enrichment. Our findings broadened discussions on maar volcanism associated with carbonate precipitation and provide insights into CO₂-related geochemical interactions in maar lake systems.

The Monoun Maar Volcano

The MMV is in the Noun Plain, a complex Quaternary volcanic field within the CVL. Situated in the western part of the Foubot volcanic field of the Noun plain (latitude 05°35'N and longitude 10°35'E) along the CVL, the MMV (Figure 1) is characterized by a large irregular maar crater comprising three WSW-ENE coalesced craters housing Lake Monoun [12, 42]. The lake has an estimated surface area of 0.62 km²; a perimeter of 5.37 km, with maximum depths of 46 m (western), 101 m (central), and 56 m (eastern) basins [12].

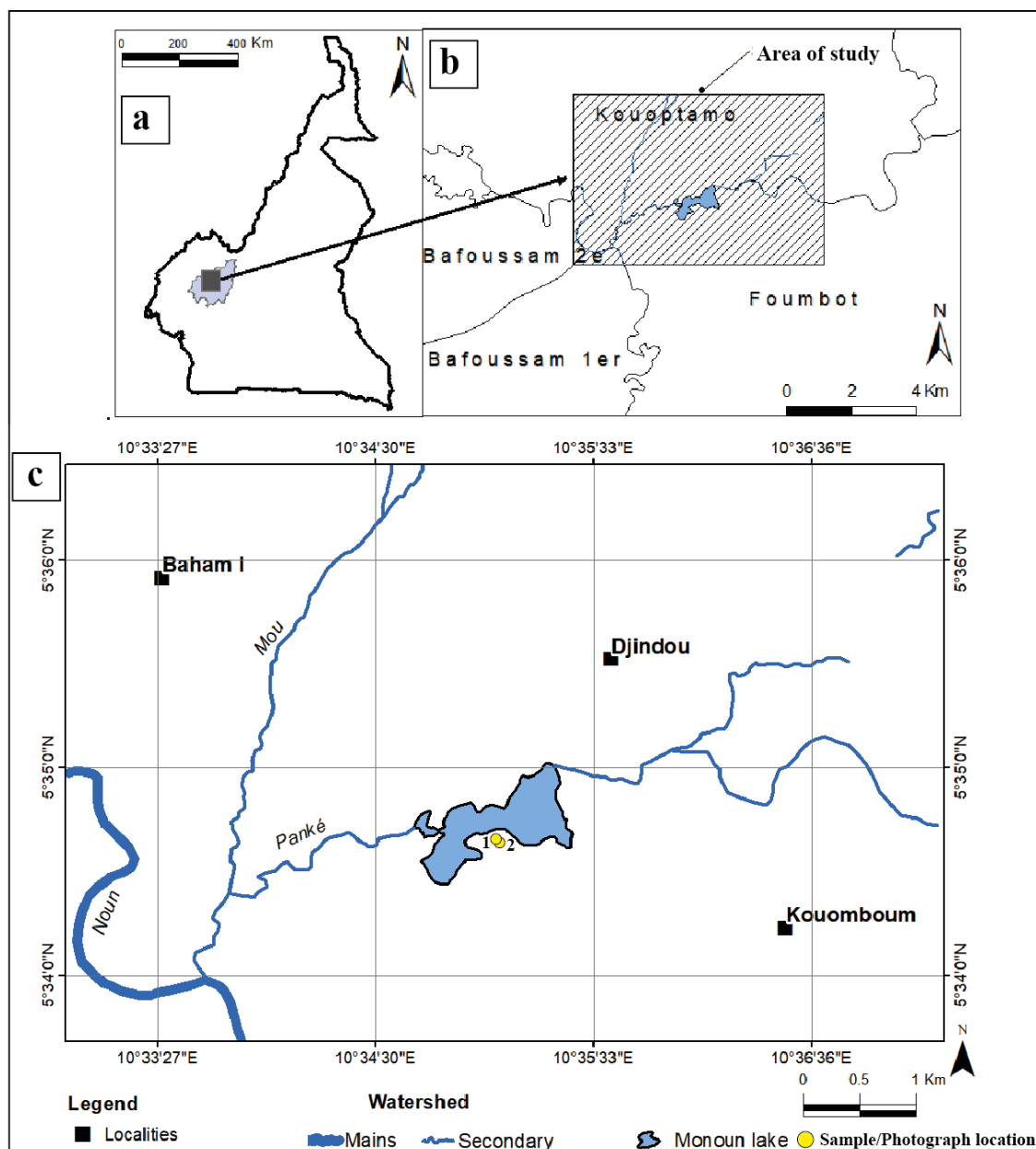


Figure 1. a) Map of Cameroon showing the West region; b) Location (box) of the MMV in the West region; c) Hydrographic Map of the MMV. Sample and photograph locations (1 [MB57]; 1 [MB58]) are shown on an embedded hydrographic map.

The MMV cut through the Precambrian basement complex, comprising fractured and weathered gneisses, migmatites, and granites and trachytes intruding amphibolites [21, 37, 50].

Overlying these formations are Quaternary volcanic lava flows (basalts and rhyolites), pyroclastic surge deposits, and pyroclastic fall deposits, indicative of episodic volcanic ac-

tivity.

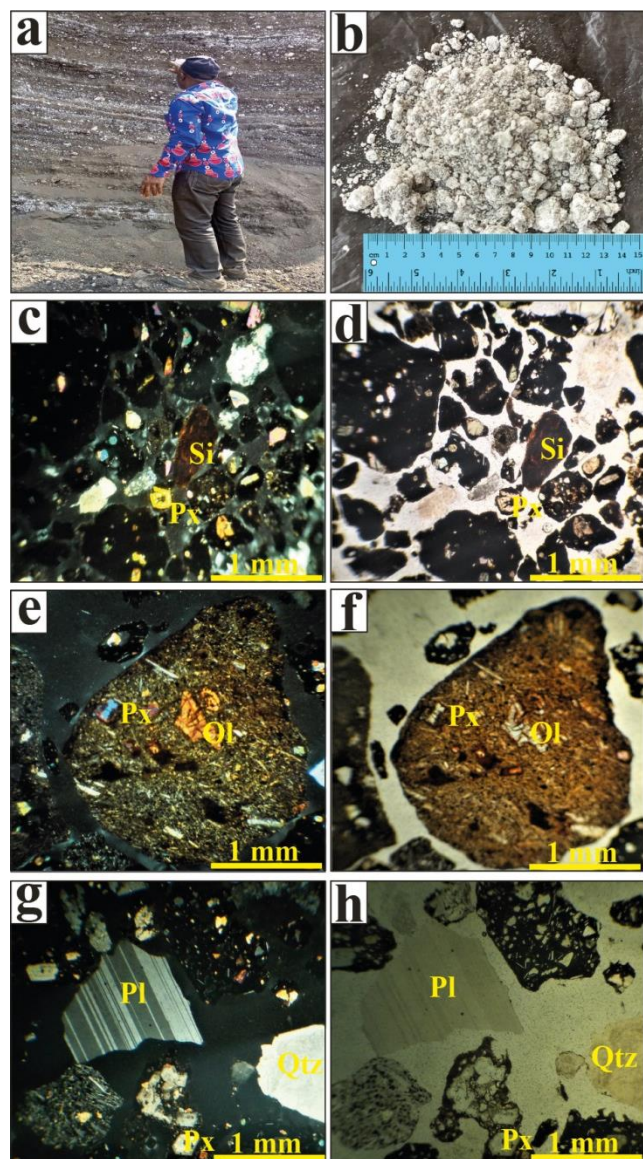


Figure 2. Photographs and photomicrographs of Siderite showing spherulitic textures in cross polarized and plane polarized light: a) outcrop, b) hand specimen, c), d), e), f), g), and h) showing massive aggregates of siderite (Field of view: 4x).

Tephrostratigraphic studies reveal that the crater walls consist of exposed tephra and lava flows, with the highest peak at 1162 m.a.s.l. on its southern flank. The deposit sequence can be divided into 7 stratigraphic units from top to bottom [37], the NW part comprising of a pyroclastic surge (unit A) resting on a thick paleosol and overlain by weathered scoria fall (unit B) and vesicular lava flow (unit C) having xenoliths of the basement and phenocrysts of olivine and pyroxene. In the SE part, the sequence continues with unit D

(Figure 2a) which comprises of three sub-units with variable amounts of carbonate precipitates occurring as encrustations on the pyroclastics (alternating lapilli ash and tuff, coarse tuff breccia, lapilli), unit E (medium tuff breccia) [Kouokam et al., in preparation], unit F (fresh scoria fall), and unit G (voluminous pyroclastic surge). There is a thin paleosol layer between the lava flow (unit C) and the scoria fall (unit F) in the NW part [37].

2. Methods

2.1. Thin Sections Preparation

Polished thin sections of the unconsolidated pyroclasts were prepared to identify the primary types of carbonates in two distinct layers forming the siderite-rich unit. Grain mounts were created at Vancouver Petrographics in Canada. This process involved embedding the bulk loose sample in a polyester resin, mixing it in plasticware, and cutting and polishing it using minor modifications of standard hard rock thin sectioning equipment and techniques. The slides were then observed with a light microscope under plane-polarized light and cross-polarized light in the Geology laboratory of the Higher Teacher Training College, The University of Bamenda.

2.2. Stable Carbon and Oxygen Isotopic Ratios Measurement

With the aid of a pocketknife, about 20 g of carbonate was collected by randomly picking coarse pyroclasts from each of the bulk samples collected from the two layers as indicated above, and scraping off the carbonate encrustations onto a piece of paper, ensuring only the collection of the carbonate encrustations (Figure 2b). These were then packed and sent for $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ isotopic analyses. The analytical procedure involved powdering about 1mg of material, which was then reacted with 100% anhydrous phosphoric acid in a vacuum chamber at 72 °C for 4 hours. The CO_2 released was analysed using a Thermo-Finnigan Delta^{plus}XP Continuous-Flow Isotope-Ratio Mass Spectrometer (CF-IRMS) coupled to a Thermo-Finnigan Gas Bench II. The $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values are reported in Table 1 using the delta (δ) notation in permille (‰), relative to Vienna Pee Dee Belemnite (VPDB) and Vienna Standard Mean Ocean Water (VSMOW), respectively, with precisions of 0.1‰ for $\delta^{13}\text{C}$, and 0.4‰ for $\delta^{18}\text{O}$. The analyses were performed at the Facility for Isotope Research, Department of Geological Sciences, Queen University, Canada.

Table 1. Stable Isotopic composition (‰) of iron carbonate samples of the Monoun Maar Volcano.

Sample	$\delta^{13}\text{C}_{\text{VPDB}}$	$\delta^{18}\text{O}_{\text{VSMOW}}$	$\delta^{18}\text{O}_{\text{VPDB}}$	Z (‰)	T (°C)
MB57	-5.2	32.3	1.38	117.34	247.93
MB58	-6.0	31.4	0.47	115.25	248.03

3. Results

3.1. Petrography

Macroscopically, samples of the carbonates from the MMV exist as whitish encrustations on the pyroclastic deposits (Figure 2a and 2b). Microscopically, siderite (Si) occurs as pale yellow-brown massive aggregates within or at the border of some clasts (Figure 2c-h). In addition, the samples have crystals of pyroxene (Px), plagioclase (Pl), and olivine (Ol).

3.2. Stable C-O Isotopic Compositions

The $\delta^{13}\text{C}_{\text{VPDB}}$, $\delta^{18}\text{O}_{\text{VSMOW}}$, and $\delta^{18}\text{O}_{\text{VPDB}}$ values of siderite in the pyroclastic of the MMV range from -6.0 to -5.2‰, 31.4 to 32.3‰, and 0.47 to 1.38‰, respectively (Table 1). Values for $\delta^{18}\text{O}_{\text{VPDB}}$ are based on Coplen et al. [6] as follows:

$$\delta^{18}\text{O}_{\text{VPDB}} = 0.970028 \delta^{18}\text{O}_{\text{VSMOW}} - 29.98 \quad (1)$$

4. Discussion

4.1. Origin of the Iron in Siderite

Previous studies suggest that the tephra dispersed around MMV is infertile due to the high amounts of siderite found in the derived soil [32]. This was corroborated by Sigurdsson et al. [42] who suggested that the crater floor sediments contained unusually high Fe^{2+} levels, which were attributed to the reduction of laterite-derived ferric iron gradually input into the lake, implying an allogenic origin.

Several studies in the world propose that the origin of iron-forming siderite in volcanic tephra result from:

- weathering of Fe-rich rocks which were uplifted near coal-bearing basins [41];
- leaching of the basement basin [18];
- rapid interaction between hydrothermal fluids/magmatic gases and volcanic ash falling into the basin [44];
- pyroclastic rocks subjected to hydrothermal alteration immediately after ashfall deposition [55], with the hydrothermal solutions either being heated-meteoric solutions with temperatures between 25-50 °C and 200 °C [7, 36] or ascending hydrothermal fluids with temperatures above 200 °C [14].

Due to the volcanic origin of the MMV deposits, the origin of iron in the siderite could correspond to options c or d.

Several lines of observations suggest that option (d), which argues for hydrothermal alteration of the pyroclastic materials immediately after ashfall, isn't likely plausible here. For example, the siderite encrustations are found only in one unit, while tephra layers above and below this unit lack their presence [Kouokam et al., in preparation]. The siderite incrustations are not concentrated in a single layer, but rather diffusively distributed in the deposits (Figure 2). The probable source and the flowing paths of the hydrothermal fluids responsible for such a siderite distribution within a deposit in dry conditions cannot be traced, hence precluding option (d) as a viable process for any authigenic origin for the studied siderites.

On the other hand, option (c) requires that tephra from previous eruptive episodes, which occurred at the start of the formation of the MMV, fell back in the crater. These were then affected by hydrothermal fluids over a long period (for example, hot fluids produced by the heat transfer from the cooling dike that fed the first eruptive episode or a chimney beneath the crater). Issa et al. [20] assumed that the majority of the measured magmatic CO_2 -flux from the MMV was produced by the oxidation of siderites that are currently found at the bottom of the lake, suggesting that volcanic activity and/or magma degassing persists at depth.

As mentioned earlier, Lake Monoun present conditions such as elevated CO_2 Supply, influx of hydrothermal fluids capable of leaching the surrounding volcanic rocks to produce Fe or directly venting Fe into the lake bottom, but also creating favourable geochemical conditions (stratification that enhance anoxic environment, influx of acidic volcanic gases (like SO_2 , HCl) that lowers the pH, and hydrothermal fluids that increases the bottom water temperatures).

^{14}C analysis depicts the source of the lake carbon to be most likely 90% from volcanic exhalations within the crater [20, 42]. Fouepe et al. [12] corroborated this by identifying two depressions on the eastern crater floor of the MMV as the major gas feeding source, with the absence of a sonar signal of CO_2 bubble rise suggesting the gas entering into a dissolved state in the lake water.

4.2. Origin of Carbon and Oxygen in Siderite

Studies by [13, 20, 26, 27, 42] demonstrated that deep waters of the MMV are dominantly composed of CO_2 with

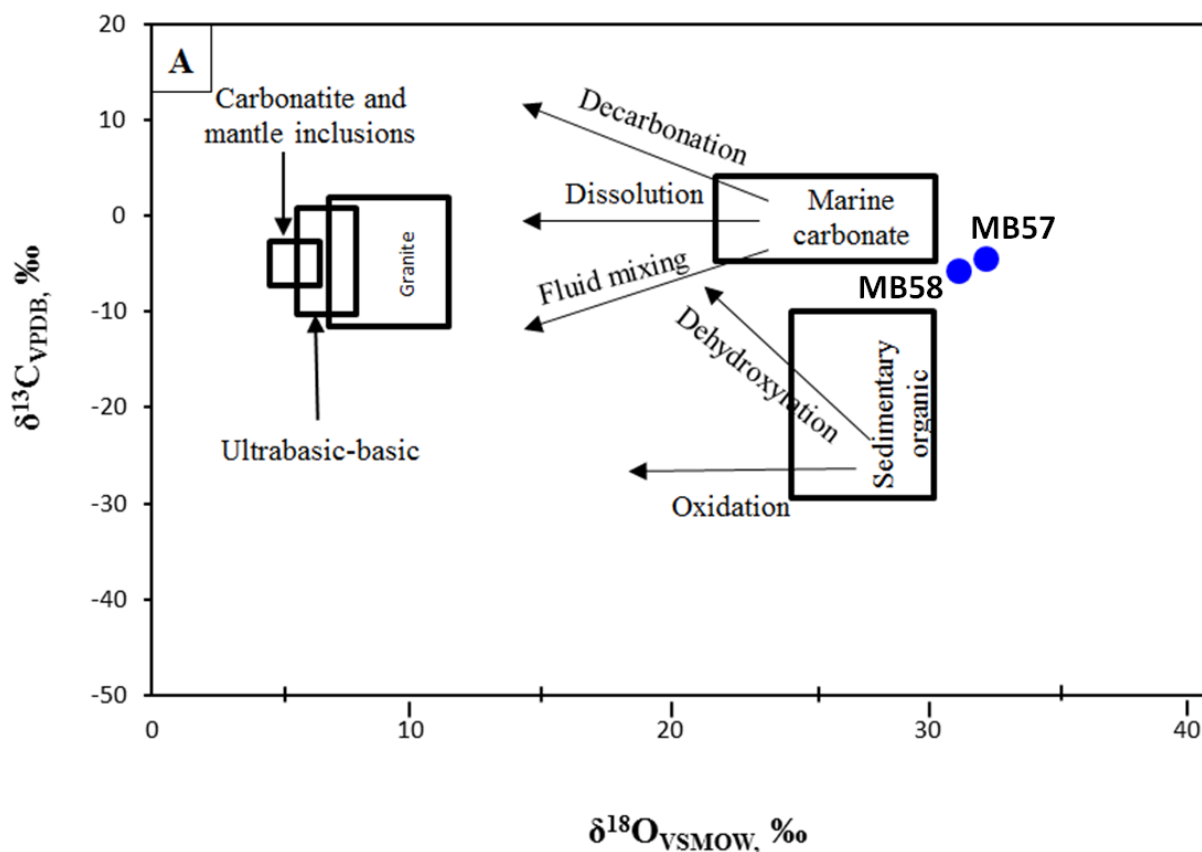
minor CH_4 , having $\delta^{13}\text{C}$ values in the range of -9.16 to -3.4 and -54.8, respectively. In addition, the ^{14}C of the lake waters indicates that only 10% of the carbon is modern, hence giving an apparent age of 18000 years. All these findings attribute the great majority of the source of carbon within the lake to long-term emissions of CO_2 from volcanic exhalation from vents within the crater. They also corroborated the study of Fouepe et al. [12] regarding the small depressions containing high concentrations of CO_2 -enriched fluids (> 82.5%) on the east and south walls of the eastern basin, representing the gas feeding source beneath the lake. In addition, the absence of the sonar signal of CO_2 bubble rise at this depression suggests that the gas is entering the lake in a dissolved state in the water, hence implying that sediments or eruptive deposits may be covering the conduct of CO_2 at these points.

Derry et al. [10] and Kaufman et al. [22] suggested that the oxygen isotopic composition of carbonate samples is relatively sensitive to the effects of temperature alteration when exposed to atmospheric conditions, strong tectonic movements and hydrothermal activity for long periods, hence, will not preserve original information of the source. To this end, it is generally accepted that a $\delta^{18}\text{O}_{\text{VPDB}} > -5\text{‰}$ indicates the unaltered nature of the rock, $\delta^{18}\text{O}_{\text{VPDB}}$ between -5 and -10‰ indicates light alteration, while a $\delta^{18}\text{O}_{\text{VPDB}} < -10\text{‰}$ indicates strongly altered rock. The calculated $\delta^{18}\text{O}_{\text{VPDB}}$ values of the analysed samples in this study range from 0.47 to 1.38 (Table 1), suggesting the unaltered nature

of the samples.

The combined study of carbon and oxygen isotopic composition in carbonate deposits represents a powerful method to fingerprint carbonates of different origins. The sources of carbon and oxygen include sedimentary organic matter, marine carbonate, hydrothermal and skarn carbonate, mantle-derived carbonates, and atmospheric carbonates [1, 9, 11, 15, 17, 34, 38, 46, 56, 57]. Generally, the $\delta^{13}\text{C}_{\text{VPDB}}$ and $\delta^{18}\text{O}_{\text{VSMOW}}$ values ranges from -30 to -10‰ and 24 to 30‰ respectively in sedimentary organic matter [15], from -4 to 4‰ and 20 to 35‰ respectively in marine carbonate [38], from -10 to 4‰ and 6 to 12‰ respectively in mantle-derived fluids [9, 46], from -20 to 4‰ and 2 to 40‰ respectively in hydrothermal and skarn ores [3, 35].

According to the modelling in Figure 3a ($\delta^{13}\text{C}_{\text{VPDB}}/\delta^{18}\text{O}_{\text{VSMOW}}$ diagram) designed to identify carbon and oxygen in carbonates of different sources, the studied samples do not show any corresponding type of carbonate but are just closer to the carbonates of marine origin and organic origin, suggesting their authigenic and allogenic nature. Figure 3b indicates that the carbon and oxygen in the carbonates derived mainly from modern soil carbonates, confirming the accuracy of the analysis and the suitability of the diagram, and that of Figure 3c which suggests carbonate from chimneys and veins precipitated from fresh and evolved meteoric waters influenced by deep CO_2 fluids.



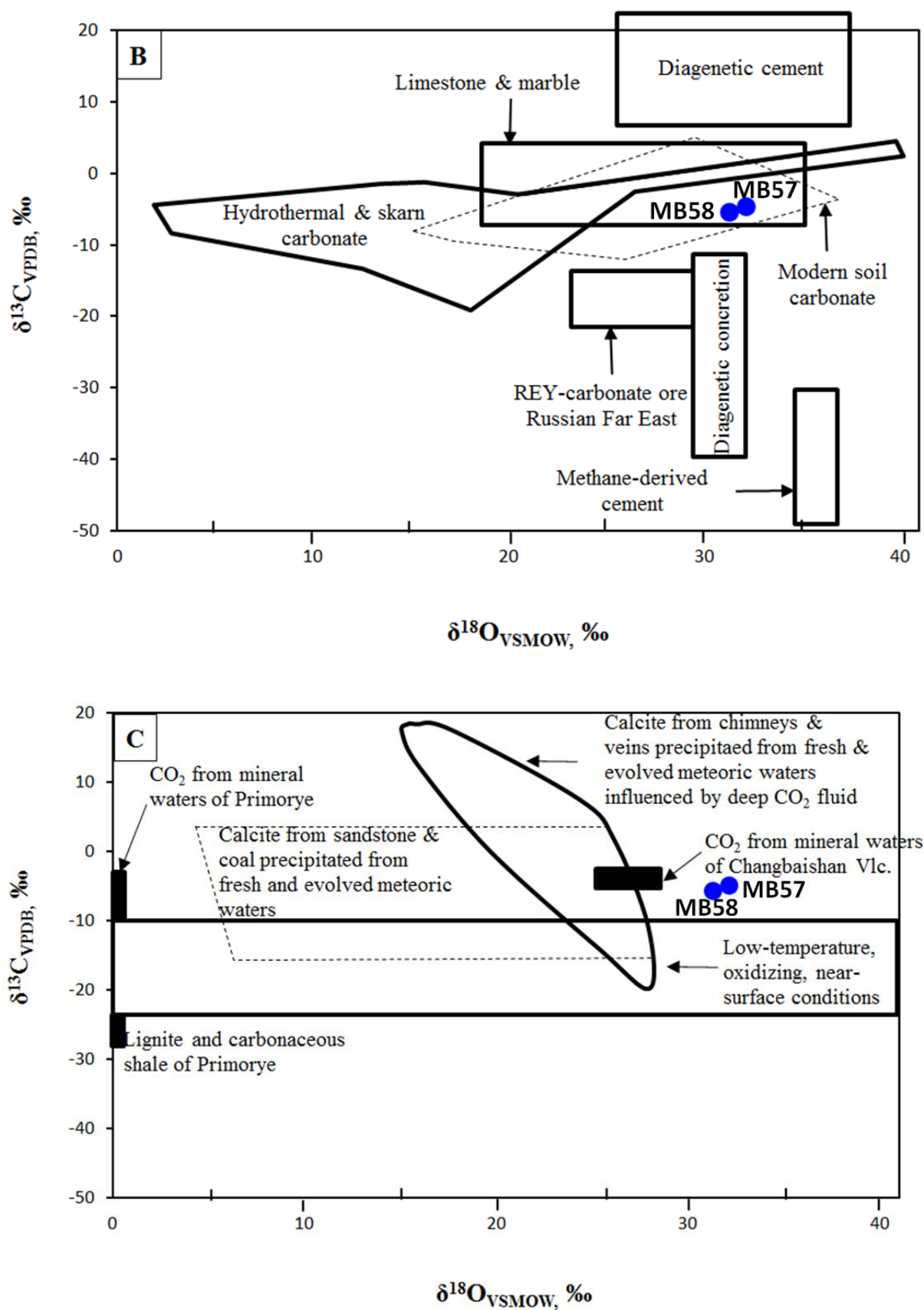


Figure 3. The $\delta^{13}\text{C} / \delta^{18}\text{O}$ discrimination diagrams showing the isotopic composition of siderite in unconsolidated tephra of the Monoun Maar Volcano: a) modified from [17, 55]; b) after [38] with additions from [3, 4, 36]; c) after [8] with additions from [5, 35]. Sample IDs (MB57; MB58) are embedded on the graphs.

4.3. Palaeoenvironment Conditions

Many authors have ventured into determining the palaeosalinity (Z) and palaeotemperature (T) of the waters associated with the formation of carbonates (calcite and siderite) in rocks and pyroclastic ejecta, using of the isotopic composition data of carbon and oxygen [28, 49, 51]. For instance, Keith and Weber [23] proposed that the Z for marine and freshwater carbonate rocks from the Jurassic and subsequent eras can be delimited based on the $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values as follows:

$$Z = 2.048 (\delta^{13}\text{C} + 50) + 0.498 (\delta^{18}\text{O} + 50) \quad (2)$$

with values of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ relative to the VPDB standard. As a result, if $Z > 120$, it depicts a marine phase, and $Z < 120$ depicts the freshwater phase. Therefore, because the studied samples are in a Quaternary volcanic field [50], no age correction is necessary as suggested by Keith and Weber [23]. The results of the Z calculated by Equation (2) yield values of 117.34 (MB57) and 115.25 (MB58), asserting a freshwater environment. According to Schopf [39], the range of $\delta^{13}\text{C}$ values for carbonate rocks originating from different sources varies from -15 to -5‰ for freshwaters and from -5 to 5‰ for marine waters. The results of this study show $\delta^{13}\text{C}$ values ranging from -6.0 to -5.2‰, corroborating a freshwater environment. Although this conclusion supports the idea, the thermal conditions necessary for the formation of the siderite remain a key factor in understanding their origin and the relationship with the eruptive history of the volcano.

Several studies have demonstrated that temperature has a significant effect on the oxygen isotope [49, 51, 54], making it possible to calculate the palaeotemperature of oxygen using the empirical formula Equation (3) of Shackleton [40]:

$$T (^{\circ}\text{C}) = 16.9 - 4.38 (\delta^{18}\text{O}_c - \delta^{18}\text{O}_w) + 0.10 (\delta^{18}\text{O}_c - \delta^{18}\text{O}_w)^2 \quad (3)$$

where $\delta^{18}\text{O}_c$ represents the value of the analysed sample relative to the VPDB standard, and $\delta^{18}\text{O}_w$ represents the value of the analysed sample relative to the VSMOW standard. Compared to the calculation of Z, the $\delta^{18}\text{O}$ values in this equation do not require age correction for the samples as they are unaltered ($\delta^{18}\text{O}_{\text{VPDB}} > -5\text{‰}$, see Table 1).

The results of the T calculated by Equation (3) show that the environmental temperature that prevailed during the formation of the studied siderites ranges between 247.93 °C (MB57) and 248.03 °C (MB58).

This result corroborates the volcanic origin (Figure 3b), an indication of high temperature carbonate-rich hydrothermal or magmatic-hydrothermal fluids emanating from the submerged volcanic vent with temperatures above 200 °C [14] which participated in the generation of a significant amount of siderite, as previously thought off in the previous studies [12, 42]. The heat could come from the cooling dike that fed the preceding eruption, but also from the magma degassing and CO_2 seepage at the bottom of the lake.

4.4. Genetic Model for Siderite Enrichment and Implications for the Eruptive Evolution of the MMV

The following genetic model may be suggested to elucidate the origin of the siderite in the localised pyroclastic ejecta at MMV. Before the formation of the siderite-rich deposits, the first volcanic episode resulted to the formation of units A (surge), B (weathered scoria) and C (lava flow). This initial phase of the eruptions was later accompanied by a period of quiescence (0.1-0.3 cal. ka; [11]) during which magma degassing favoured the formation of siderite. Some of the pyroclastic ejecta, together with the allochthonous sediments, were brought into the deeper parts of the eastern basin. This formed a natural seal that prevented the escape of magmatic CO_2 into the lake water, followed by overpressurization. Solutions began to boil, separating gas-rich vapours, accumulating and forming gas pockets with steadily increasing pressures. When this high gas pressure exceeded lithostatic pressure, it led to a blow-out or explosive phreatomagmatic eruptions, ejecting tephra deposits rich in siderite into the atmosphere, which later on accumulated, producing unit D rich in dispersed siderite deposits. Subsequent eruptions then followed without significant repose periods either in the western and central basins, producing tephra deposits of units E, F and G, with the clasts not possessing siderite encrustations. This could be probably due to the fact that there was no time break necessary enough for the magmatic CO_2 -flux to recharge from the sub-volcanic vents at the bottom of the crater.

5. Conclusion

This study presents a first comprehensive study on the origin of carbonate deposits within the tephra deposits of the MMV based on petrographic, isotope geochemistry, and paleoenvironmental modelling using $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$.

- 1) The $\delta^{13}\text{C}_{\text{VPDB}}$ and $\delta^{18}\text{O}_{\text{VSMOW}}$ values of siderite in the pyroclastics range from 31.4 to 32.3‰, and -6.0 to -5.2‰, respectively. This is an indication of a combination of meteoric waters (fresh water, contributing sediments rich in carbonates) and CO_2 emanating from volcanic vents.
- 2) The palaeosalinity (Z) and palaeotemperature (T) of the carbon and oxygen isotopes were calculated using the age-non corrected isotopic data. The Z values range from 115.25 to 117.34‰, whilst the T values vary from 247.93 to 248.03 °C. This is an indication the siderite originated from fresh water sources, with a great contribution of high-temperature hydrothermal or magmatic-hydrothermal CO_2 -rich fluids emanating from the eastern crater basin.
- 3) After the formation of units, A-C, the tephra ejecta together with allogenic sediments were later deposited into the eastern crater basin, forming a natural seal favouring the gradual accumulation of CO_2 -flux (over a

reposed period of 0.1-0.3 cal. ka) and also preventing the escape of these high temperature CO₂-rich fluids. This led to overpressurization, leading to phreato-magmatic eruptions ejecting tephra deposits that accumulated to form the localized unit D rich in dispersed siderite deposits. Different volcanic episodes then ensued (without a repose time), producing units, E-G, not containing siderite encrustations.

These results point to a long-term magma degassing after the first eruptions that initiated the formation of the maar, followed by a period of volcanic quiescence favouring the formation and accumulation of siderites. This was then succeeded by another eruption inside the crater ejecting the siderite-rich sediments that composed the studied deposits.

Abbreviations

MMV	Monoun Maar Volcano
CVL	Cameroon Volcanic Line
VPDB	Vienna Pee Dee Belemnite
VSMOW	Vienna Standard Mean Ocean Water
Z	Palaeosalinity
T	Paleotemperature

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Author Contributions

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Wotchoko Pierre: Conceptualization, Funding Investigation, Methodology, Project administration, Supervision, Validation, Visualization, Writing – original draft, Writing – review & editing

Cheo Emmanuel Suh: Funding acquisition, Supervision, Validation, Writing – original draft, Writing – review & editing

Chako-Tchamab é Boris: Supervision, Validation, Writing – original draft, Writing – review & editing

Chenyi Marie-Louise Vohnyui: Investigation, Supervision, Validation, Visualization, Writing – original draft, Writing – review & editing

Guedjeo Christian Suh: Investigation, Methodology, Supervision, Writing – original draft

Fantong Wilson Yetoh: Methodology, Writing – original draft, Writing – review & editing

Farouk Oumar Mouncherou: Methodology, Writing – original draft, Writing – review & editing

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Conflicts of Interest

The authors declare no conflicts of interest.

References

- [1] Allan, J. R., Mathews, R. K., 1982. Isotope signatures associated with early meteoric diagenesis. *Sedimentology*, 29, 797-817.
- [2] Aziwo, B. T., Tamen, J., Tchamab é B. C., Asaah, A. N. E., Yangouo, F. K., Dongmo, B. S. Z., Tabengo, M. Z., Tedonkenfack, S. S. -T., 2022. Tephrostratigraphy and morphometry of Wum Maar Volcano (Oku Volcanic Group-Cameroon Volcanic line): Implications for complex monogenetic volcanoes. *Journal of African Earth Sciences*, 188, pp. 19. <https://doi.org/10.1016/j.jafrearsci.2022.104470>
- [3] Bowman, J. R., 1998. Stable-isotope systematics of skarns. In: Lentz, D. R. (Ed.), *Mineralized Intrusion-Related Skarn Systems*. Mineralogical Association of Canada Short Course, 26, 99-145.
- [4] Cerling, T. E., Quade, J., 1993. Stable carbon and oxygen isotopes in soil carbonates. In: Swart, P., McKenzie, J. A., Lohman, K. C. (Eds.). *American Geophysical Union Monograph*, 78, 217-231.
- [5] Chelnokov, G. A., Kharitonova, N. A., Bragin, I. V., 2013. Composition and genesis of the gases of the carbon mineral waters in the southern part of the Russian Far East, *Izvestiya Vuzov. Geologiya i Razvedka*, 5, 42-46.
- [6] Coplen, T. B., Kendall, C., Hopple, J., 1983. Comparison of stable isotope reference standards. *Nature*, 302, 236-238.
- [7] Dai, S., Nechaev, V. P., Chekryzhov, I. Y., Zhao, L., Vysotskiy, S. V., Graham, I., Ward, C. R., Ignatiev, A. V., Velivetskaya, T. A., Zhao, L., 2018. A model for Nb-Zr-REE-Ga enrichment in Lopingian altered alkaline volcanic ashes: Key evidence of H-O isotopes. *Lithos*, 302, 359-369. <https://doi.org/10.1016/j.lithos.2018.01.005>
- [8] Dawson, G. K. W., Golding, S. D., Boreham, C. J., Mernagh, T., 2013. Authigenic carbonates as natural analogues of mineralisation trapping in CO₂ sequestration. In: *Cooperative Research Centre for Greenhouse Gas Technologies*, vols. RPT13-4602. CO₂CRC Publication Number, Canberra, Australia (75 pp).

- [9] Demény, A., Ahijado, A., Casillas, R., Vennemann, T., 1998. Crustal contamination and fluid/rock interaction in the carbonatites of Fuerteventura (Canary Islands, Spain): a C, O, H isotope study. *Lithos*, 44, 101-115. [https://doi.org/10.1016/S0024-4937\(98\)00050-4](https://doi.org/10.1016/S0024-4937(98)00050-4)
- [10] Derry, L. A., Kaufman, A. J., Jacobsen, S. B., 1992. Sedimentary cycling and environmental change in the late Proterozoic: evidence from stable and radiogenic isotopes. *Geochimica et Cosmochimica Acta*, 56, 1317-1329. [https://doi.org/10.1016/0016-7037\(92\)90064-P](https://doi.org/10.1016/0016-7037(92)90064-P)
- [11] Du, L. -J., Li, B., Huang, Z. -L., Zhou, J. -X., Zou, G. -F., Yan, Z. -F., 2017. Carbon-oxygen isotopic geochemistry of the Yangla Cu skarn deposit, SW China: Implications for the source and evolution of hydrothermal fluids. *Ore Geology Reviews*, 88, 809-821. <https://doi.org/10.1016/j.oregeorev.2017.01.026>
- [12] Fouepe, T. A., Ntchantcho, R., Saiki, K., Ohba, T., Kamtchueng, B., Tanyileke, G., Fraleu, B., Hell, J., 2019. New insights into volume estimates and gas contents from the acoustic investigation at Lake Monoun, Cameroon. *Journal of African Earth Sciences*, 160, 8pp. <https://doi.org/10.1016/j.jafrearsci.2019.103604>
- [13] Giggenbach, W. F., Sano, Y., Schmincke, H. U., 1991. CO₂-rich gases from Lakes Nyos and Monoun, Cameroon; Laechee See, Germany; Dieng, Indonesia, and Mt. Gambier, Australia-variations on a common theme. *Journal of Volcanology and Geothermal Research*, 45, 311-323. [https://doi.org/10.1016/0377-0273\(91\)90065-8](https://doi.org/10.1016/0377-0273(91)90065-8)
- [14] Guilbert, J. M., Park Jr., C. F., 1986. *The Geology of Ore Deposits*. Freeman, W. H., 4th edition, pp 985.
- [15] Hoefs, J., 2009. *Stable Isotope Geochemistry*. Berlin Heidelberg, 285, 191-207.
- [16] Houghton, B. F. and Schmincke, H. -U., 1986. Mixed deposits of simultaneous strombolian and phreatomagmatic volcanism: Rothenberg volcano, east Eifel volcanic field. *Journal of Volcanology and Geothermal Research*, 30, 117-130. [https://doi.org/10.1016/0377-0273\(86\)90069-7](https://doi.org/10.1016/0377-0273(86)90069-7)
- [17] Hu, R., Fu, S., Huang, Y., Zhou, M. -F., Fu, S., Zhao, C., Wang, Y., Bi, X., Xiao, J., 2017. The giant South China Mesozoic low-temperature metallogenic domain: Reviews and a new geodynamic model. *Journal of Asian Earth Sciences*, 137, 9-34. <https://doi.org/10.1016/j.jseas.2016.10.016>
- [18] Huang, X. -W., Qi, L., Meng, Y. -M., Chen, D., Ling, H. -D., 2015. Origin of siderite mineralization in western Guizhou, SW China: Constrains from REEs, C, O, Sr and S isotopes. *Ore Geology Reviews*, 66, 252-265. <https://dx.doi.org/10.1016/j.oregeorev.2014.11.003>
- [19] Issa, Ohba, T., Fantong, W., Fouepe, A., Tchamabé B. C., Yoshida, Y., Kusakabe, M., Sigha, N., Tsunogai, U., Oginuma, Y., Tanyileke, G., Satake, H., Hell, J. V., 2013. Contribution of methane to total gas pressure in deep waters at lake Nyos and Monoun (Cameroon, West Africa). *Geochemical Journal*, 47, 349-362. <https://doi.org/10.2342/geochemj.2.0250>
- [20] Issa, Ohba, T., Tchamabé B. C., Padrón, E., Hernández, P., Eneke Takem, E. G., Barrancos, J., Sighomnoun, D., Ooki, S., Nkamdjou, S., Kusakabe, M., Yoshida, Y., Dionis, S., 2014a. Gas emission from diffuse degassing structures (DDS) of the Cameroon volcanic line (CVL): Implications for the prevention of CO₂-related hazards. *Journal of Volcanology and Geothermal Research*, 283, 82-93. <https://doi.org/10.4081/jlimnol.2014.966>
- [21] Kamtchueng, B. T., Fantong, W. Y., Wirmvem, M. J., Tiodjio, R. E., Takounjou, A. F., Ndam, N. J. R., Kusakabe, M., Zhang, J. Ohba, T., Tanyileke, G., Hell, J. V., Ueda, A., 2016. Hydrogeochemistry and quality of surface water and groundwater in the vicinity of Lake Monoun, West Cameroon: approach from multivariate statistical analysis and stable isotopic characterization. *Environmental Monitoring and Assessment*, 524, 24pp. <https://doi.org/10.1007/s10661-016-5514-x>
- [22] Kaufman, A. J., Jacobsen, S. B., Knoll, A. H., 1993. The Vendian record of Sr and C isotopic variations in seawater: implications for tectonics and paleoclimate. *Earth and Planetary Science Letters*, 120, 409-430. [https://doi.org/10.1016/0012-821X\(93\)90254-7](https://doi.org/10.1016/0012-821X(93)90254-7)
- [23] Keith, M., Weber, J., 1964. Carbon and oxygen isotopic composition of selected limestones and fossils. *Geochimica et Cosmochimica Acta*, 28, 1787-1816. [https://doi.org/10.1016/0016-7037\(64\)90022-5](https://doi.org/10.1016/0016-7037(64)90022-5)
- [24] Kling, G. W., 1988. Comparative transparency, depth of mixing, and stability of stratification in lakes of Cameroon, West Africa. *Limnology and Oceanography*, 33(1), 27-40.
- [25] Kling, G. W., Evans, W. C., Tanyileke, G. Z., 2015. The Comparative Limnology of lakes Nyos and Monoun, Cameroon. In: Rouwet, D., Christenson, B., Tassi, F., Vandemeulebrouck, J., (eds.) *Volcanic Lakes. Advances in Volcanology*. Springer, Berlin, Heidelberg, 401-425. https://doi.org/10.1007/978-3-642-36833-2_18
- [26] Kusakabe, M., Ohsumi, T., Aramaki, S., 1989. The Lake Nyos gas disaster: chemical and isotopic evidence in waters and dissolved gases from three Cameroonian crater lakes, Nyos, Monoun and Wum. *Journal of Volcanology and Geothermal Research*, 39, 167-185. [https://dx.doi.org/10.1016/0377-0273\(89\)90056-5](https://dx.doi.org/10.1016/0377-0273(89)90056-5)
- [27] Kusakabe, M., 2015. Evolution of CO₂ content in Lakes Nyos and Monoun, and Sub-lacustrine CO₂-recharge system at Lake Nyos as envisaged from CO₂/³He ratios and Noble gas signatures. In: Rouwet, D., Christenson, B., Tassi, F., Vandemeulebrouck, J., (eds.) *Volcanic Lakes. Advances in Volcanology*. Springer, Berlin, Heidelberg, 427-450. https://doi.org/10.1007/978-3-642-36833-2_19
- [28] Li, X., Xu, W., Liu, W., Zhou, Y., Wang, Y., Sun, Y., Liu, L., 2013. Climatic and environmental indications of carbon and oxygen isotopes from the lower cretaceous calcrite and lacustrine carbonates in Southeast and Northwest China. *Palaeogeography, Palaeoclimatology, Palaeoecology*, 385, 171-189. <https://doi.org/10.1016/j.palaeo.2013.03.011>
- [29] Lorenz, V., 1973. On the formation of Maars. *Bulletin of Volcanology*, 37, 183-204.

- [30] Lorenz, V., 1985. Maars and diatremes of phreatomagmatic origin: a review. *S. Afr. J. Geol.*, 88(2), 459-70.
- [31] Lorenz, V., 1986. On the growth of maar and diatremes and its relevance to the formation of tuff rings. *Bulletin of Volcanology*, 48(5), 265-74.
- [32] Makilo, R., 1982. Etude des Sols Développés sur Matériaux Volcaniques Récents dans un secteur de L'Ouest-Cameroun (Region de Foumbot). Office de la Recherche Scientifique et Technique Outre-Mer, Mission ORSTROM Yaoundé
- [33] McClintock, M., White, J. D. L., Houghton, B. F., Skilling, I. P., 2008. Physical Volcanology of a Large Crater Complex Formed during the Initial Stages of Karoo Flood Basalt Volcanism, Sterkspruit, Eastern Cape, South Africa. *Journal of Volcanology and Geothermal Research*, 172, 93-111. <https://doi.org/10.1016/j.jvolgeores.2005.11.012>
- [34] Liu, J. M., Liu, J. J., Gu, X. X., 1997. Basinal fluid genetic model of fine disseminated gold deposits in the golden triangle area between Yunnan, Guizhou and Guangxi. *Acta Petrologica et Mineralogica*, 17, 448-456.
- [35] Nechaev, V., Chekryzhov, I. Y., Vysotskiy, S., Ignatiev, A., Velivetskaya, T., Tarasenko, I., Agoshkov, A., 2018. Isotopic signatures of REY mineralization associated with lignite basins in South Primorye, Russian Far East. *Ore Geology Reviews*, 103, 68-77. <https://doi.org/10.1016/j.oregeorev.2018.01.018>
- [36] Nechaev, V. P., Dai, S., Zhao, L., Moore, T. A., Nechaeva, E. V., 2021. The Tarim Basin, China, a prospect for plume-related Zr (Hf)-Nb (Ta)-REY-Ga-U mineralization. *Ore Geology Reviews*, 133, 104081. <https://doi.org/10.1016/j.oregeorev.2021.104081>
- [37] Nche, L. A., Hasegawa, T., Aka, F. T., Ohba, T., Mafany, G. T., Németh, K., Miyabuchi, Y., Asaah, A. N. E., Wajiba, P. M., Ngwa, C. N., Tchop, J. L., Nguet, P. W., Nfomou, N., Suh, C. E., Fantong, W. Y., Mouncherou, F. O., 2025. Volcanic history and magma systems of Lake Monoun Polygenetic Maar, Noun Plain, Western part of the Cameroon Volcanic Line: Constraints from stratigraphy, chronology and dgeochemistry. *Journal of Volcanology and Geothermal Research*, 460, 108265. <https://doi.org/10.1016/j.jvolgeores.2025.108265>
- [38] Rollinson, H. R., 1993. Using Geochemical Data: Evaluation, Presentation, Interpretation. Longman Scientific and Technical Press, Wiley, New York, pp 352.
- [39] Schopf, T. J. M., 1980. Paleooceanography. Harvard University Press, Cambridge, MA (figs, tables) 341 pp.
- [40] Shackleton, N. J., 1975. Paleotemperature history of the Cenozoic and the initiation of Antarctic glaciation: oxygen and carbon isotope analyses in DSDP Sites 277, 279, and 281. In: Initial Reports of Deep Sea Drilling Project, 29, 743-756.
- [41] Shen, Y., Qin, Y., Li, Z., Jin, J., Wei, Z., Zheng, J., Zhang, T., Zong, Y., Wang, X., 2017. The sedimentary origin and geological significance of siderite in the Longtan Formation of western Guizhou Province. *Earth Science Frontiers*, 24, 152-161.
- [42] Sigurdson, H., Devine, F. M., Tchoua, T. S., Pringle, M. K. W., Evans, W. C., 1987. Origin of the lethal gas burst from lake Monoun, Cameroon. *Journal of Geothermal Research*, 31, 1-16. [https://doi.org/10.1016/0377-0273\(87\)90002-3](https://doi.org/10.1016/0377-0273(87)90002-3)
- [43] Stix, J. and de Moor, J. M., 2018. Understanding and forecasting phreatic eruptions driven by magmatic degassing. *Earth, Planets and Space*, 70(83), 19 pp. <https://doi.org/10.1186/s40623-018-0855-z>
- [44] Sturesson, U., Heikoop, J., Risk, M., 2000. Modern and Palaeozoic iron ooids-a similar volcanic origin. *Sedimentary Geology*, 136, 137-146. [https://doi.org/10.1016/S0037-0738\(00\)00091-9](https://doi.org/10.1016/S0037-0738(00)00091-9)
- [45] Tanyileke, G., Ntchantcho, R., Fantong, W. Y., Aka, F. T., Hell, J. V., 2019. 30 years of the Lakes Nyos and Monoun gas disasters: A scientific, technological, institutional and social adventure. *Journal of African Earth Sciences*, 150, 415-424. <https://doi.org/10.1016/j.jafrearsci.2018.11.022>
- [46] Taylor, J., H. P., Frechen, J., Degens, E. T., 1967. Oxygen and carbon isotope studies of carbonatites from the Laacher See District, West Germany and the Aln District, Sweden. *Geochimica et Cosmochimica Acta*, 31, 407-430. [https://doi.org/10.1016/0016-7037\(67\)90051-8](https://doi.org/10.1016/0016-7037(67)90051-8)
- [47] Tchamabé B. C., Youmen, D., Owona, S., Issa, Ohba, T., Németh, K., Ngapna, M. S., Asaah, A. N. E., Aka, F. T., Tanyileke, G., Hell, J. V., 2013. Eruptive history of Barombi Mbo maar, Cameroon Volcanic Line, Central Africa: Constraints from volcanic facies analysis. *Central European Journal of Geosciences*, 5(4), 480-496. <https://doi.org/10.2478/s13533-012-0147-2>
- [48] Tchamabé B. C., Ohba, T., Kereszturi, G., Németh, K., Aka, F. T., Youmen, D., Issa, Miyabuchi, Y., Ooki, S., Tanyileke, G., Hell, J. V. 2015. Towards the reconstruction of the shallow plumbing system of the Barombi Mbo Maar (Cameroon): Implications for diatreme growth processes of a polygenetic maar volcano. *Journal of Volcanology and Geothermal Research*, 301, 293-313. <http://dx.doi.org/10.1016/j.jvolgeores.2015.06.004>
- [49] van Dijk, J., Fernandez, A., Müller, I. A., Lever, M., Bernasconi, S. M., 2018. Oxygen isotope fractionation in the siderite-water system between 8.5 and 62 °C. *Geochimica et Cosmochimica Acta*, 220, 535-551. <https://doi.org/10.1016/j.gca.2017.10.009>
- [50] Wandji, P., 1995. Le volcanisme récent de la plaine du Noun (Ouest-Cameroun). *Volcanologie, Pétrologie, Géochimie et Pouzzolanité Thèse Doctorat d'Etat de L'Université Yaoundé I, Cameroun*, pp. 295.
- [51] Wang, N., Dai, S., Nechaev, V. P., French, D., Graham, I. T., Zhao, F., Zuo, J., 2022. Isotopes of carbon and oxygen of siderite and their genetic indications for the Late Permian critical-metal tuffaceous deposits (Nb-Zr-REY-Ga) from Yunnan, southwestern China. *Chemical Geology*, 592, 120727. <https://doi.org/10.1016/j.chemgeo.2022.120727>
- [52] White, J. D. L. and Ross, S. P., 2011. Maar-diatreme volcanoes: A review. *Journal of Volcanology and Geothermal Research*, 201(1-4), 1-29. <http://dx.doi.org/10.1016/j.jvolgeores.2011.01.010>

- [53] Wohletz, K. H. and Sheridan, M. F., 1983. Hydrovolcanic explosions II. Evolution of basaltic tuff rings and tuff cones. *American Journal of Science*, 283, 385-413.
- [54] Zhang, G., 1997. Analysis of paleoenvironment and sea level change using sedimentary geochemical characteristics: A case study of the Middle and Lower Cambrian in eastern Shandong Province. *Land and Resources*, 9-13.
- [55] Zhao, L., Dai, S., Graham, I. T., Li, X., Liu, H., Song, X., Hower, J. C., Zhou, Y., 2017a. Cryptic sediment-hosted critical element mineralization from eastern Yunnan Province, southwestern China: Mineralogy, geochemistry, relationship to Emeishan alkaline magmatism and possible origin. *Ore Geology Reviews*, 80, 116-140. <https://doi.org/10.1016/j.oregeorev.2016.06.014>
- [56] Zhou, J. -X., Huang, Z. -L., Lv, Z. -C., Zhu, X. -K., Gao, J. -G., Mirnejad, H., 2014. Geology, isotope geochemistry and ore genesis of the Shanshulin carbonate-hosted Pb-Zn deposit, Southwest China. *Ore Geology Reviews*, 63, 209-225. <https://doi.org/10.1016/j.oregeorev.2014.05.012>
- [57] Zhuo, Y., Hu, R., Xiao, J., Zhao, C., Huang, Y., Yan, J., Li, J., Gao, W., Li, J., 2019. Trace elements and CO isotopes of calcite from Carlin-type gold deposits in the Youjiang Basin, SW China: Constraints on ore-forming fluid compositions and sources. *Ore Geology Reviews*, 113, 103067. <https://doi.org/10.1016/j.oregeorev.2019.103067>