Citation for final published version:

Fantong, Wilson Yetoh, Kamtchueng, Brice Tchakam, Ishizaki, Yasuo, Chi Fru, Ernest , Fantong, Emilia Bi, Wirmvem, Mengnjo Jude, Tongwa AKA, Festus, Nlend, Bertil, Harman, Didier, Ueda, Akira, Kusakabe, Minoru, Tanyileke, Gregory, Ohba, Takeshi and Fru, Ernest Chi 2019. Major ions, δ18O, δ13C and 87Sr/86Sr compositions of water and precipitates from springs along the Cameroon Volcanic Line (Cameroon, West Africa): Implications for provenance and volcanic hazards. Journal of African Earth Sciences 150 , pp. 12-22. 10.1016/j.jafrearsci.2018.09.025

Publishers page: http://dx.doi.org/10.1016/j.jafrearsci.2018.09.025

Elsevier Editorial System(tm) for Journal of African Earth Sciences
Manuscript Draft

Manuscript Number: AES6311R2

Title: Major ions, δ18O, δ13C and 87Sr/86Sr compositions of water and precipitates from springs along the Cameroon Volcanic Line (Cameroon, West Africa): Implications for provenance and volcanic hazards

Article Type: VSI:Lake Nyos,30 years after

Keywords: Bubbling springs. Precipitates. Composition. Provenance. Volcanic activity. Hazards mitigation.

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NOTE TO EDITOR AND REVIEWERS

(1) We modified the title slightly to make it sharper, shorter and punchier (the modified version is in BLUE colour)

(2) Apart from the review comments, we saw a few editing issues in the text and corrected. Find them in BLUE colour

(3) Reactions to Editor and Reviewers comments are in RED

Responses to editor and reviewers comments

RESPONSE TO EDITOR AND REVIEWERS

L. 28: contained = contains : **Corrected on line 28**

L. 55-56: Order references in chronological order (also L. 84 and check throughout the MS) : References have been ordered chronologically in the entire MS. Example is shown on line 81

L. 76: add "." At end of sentence (also for L. 396) : Added

L. 78-79. Split this sentence in two sentences for clarity : **Sentence has been modified for clarity on lines 76-79**

L. 97. Warmness = heating : **Corrected on line 93**

L. 100-101. Form of the use of Figure or Fig. (editing issue) : **Form corrected**

L. 138. Impact = impacts : Corrected on line 131

L. 150. Delete "very" : **Deleted**

L. 176. Delete "," after "Fantong et al." **Deleted on line 168**

L. 178. Delete "(…)" in Davies reference : **Deleted on line 169**

L. 189. Stoichemistry? Is this correct + Faure, 1991 (add ",") (same for L. 198 Appelo and Postman, 2005 + L. 222 + L. 348) **: All corrections done**

L. 216. Delete space before "were" (also for L. 374 before "whilst") : Corrected

L. 227. Field "of" kaolinite (add "of) : **Corrected on line 218**

L. 262 + 271. Almost absence. Try to find another expression : Alternative expression used on lines 257 and 267

L. 285. Mid-1900s : Corrected on line 282

L. 298-299. Is T expressed in °C or K, please mention : ºC, mentionned on line 297

L. 317. Delete "ocean-continental boundary" (as it is already defined before) : **Deleted**

L. 350 Kusakabe (2017): add the "(…)" **: added on line 346**

L. 355. "… when the system". This sentence lost its structure, please check and rephrase. **Has been checked and corrected**

L. 352-357: I don't know if this part is strictly necessary to tell your story, although it is obviously correct to say so. Up to you. It comes a bit out o the blue, as I think "magmatic degassing" sounds "volcanic", too volcanic for the system we have here. **Per the first reviewer comment, i think it is necessary because it gives more justification for monitoring**

L. 359. law = low : **Corrected on line 355**

L. 360. Carbondioxide = CO2 on line 357

L. 373. Fluorine = origin : **Corrected**

Fig. 18. Liotta et al. (2016) = Liotta et al. (2017) : **Corrected on Fig. 18**

Tables. Red colour should be black. Changed in Table 1

Specific comment.

I suggest you add the chemical formula for trona and dolomite the first time you use it in the text (or table) : **Chemical formulae of trona and dolomite introduced in abstract (lines 30 and 31)**

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Major ions, $\delta^{18}O$, $\delta^{13}C$ and $^{87}Sr/^{86}Sr$ compositions of water and precipitates from springs along the Cameroon Volcanic Line (Cameroon, West Africa): Implications for provenance and volcanic hazards

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Abstract

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Introduction

Mineral-depositing springs are natural systems that offer a good opportunity to study various mechanisms by which waters establish equilibrium with conditions at the Earth's surface (Amundson and Kelly, 1987; Omelon et al., 2006). For example, carbonate-precipitating waters provide an opportunity to evaluate a dynamic carbonate system and the major controls associated with calcite precipitation (Barnes, 1965; Jacobson and Usdowski, 1975), including; isotope fractionation associated with natural calcite precipitation from spring waters (McCrea, 1950; Friedman, 1970; Usdowski et al., 1979; Dandurand et al., 1982; Amundson and Kelly,1987; Usdowski and Hoefs, 1990; Hamilton et al.,1991; Liu et al., 2003), as well as the types, morphologies, textures, and processes involved in the formation of various carbonate phases (Tucker and Bathurst, 1990; Bradley and Eugster, 1969; Ford and Pedley, 1996; Forti, 2005).

Many orifices of gas-water-carbonate interacting systems occur along the Cameroon Volcanic Line (CVL-Fig. 1). Based on carbonate enrichment studies on volcanic debris and springs in part of the continental sector of the CVL (Le Marechal, 1976; Verla et al., 2014); chemical and isotopic characteristics of fluids along the CVL (Tanyileke , 1994); the geochemistry of gases in springs around Mt. Cameroon and Lake Nyos (Kusakabe et al., 1989; Sano et al.,1990; Aka, 1991); the sedimentology and geochemistry of the Bongongo and Ngol travertines along the CVL (Bisse et al., 2018), the following hypotheses have been proposed: (1) the bubbling mineral springs along the CVL contain abundant CO_2. (2) The CO_2 in the bubbling springs is dominantly of magmatic origin. (3) Helium and carbon isotope ratios of gases from a few of the springs

along the CVL revealed a signature similar to hotspot type magma. (4) The precipitating minerals are travertines.

Although these studies provide initial data to understand the geochemical dynamics within the CVL gas-water-carbonate systems, gaps required to better understand the system include; a) a total absence of comprehensive information on the classification and genetic processes of the precipitating carbonates, which is exploited by the indigenes for preparation of traditional soup, b) high concentration (> 100 mg/l) of geogenic fluoride has been reported (e.g., Kut et al., 2016; and references there-in) in thermal waters along the Ethopian rift. Such concentrations of fluoride in water that is used for domestic purposes and livestock rearing can cause tremendous health effects (e.g., Fantong et al., 2010). Livestock rearing on the slopes of the CVL heavily consumes water from the springs (Fig. 2), so there is still a need to re-assess their chemical characteristics with focus on potential harmful elements like fluoride and arsenic, and c) the carbonate-water fractionation temperature remains unknown.

Against this backdrop, the objectives of this study are to 1) characterize the water chemistry with focus on health implications, 2) estimate the carbonate-water fractionation temperature, and 3) identify, describe and classify the carbonates that are precipitating from the springs.

Study area

Figure 1 shows, the sample sites along the CVL, a prominent 1600 km long Y-shaped chain of Tertiary to Recent, generally alkaline volcanoes that overlap an array of dextral faults called the Central Africa Shear Zone (CASZ) (Ngako et al., 2006) on the African continent, comparable only to the East Africa Rift System. The CVL follows a trend of crustal weakness that stretches from the Atlantic Island of Annobon, through the Gulf of Guinea, to the interior of the African continent (Fitton, 1980; Déruelle et al., 1987, Halliday et al., 1988;). It is unique amongst intraplate volcanic provinces in that it straddles the continental margin and includes both oceanic and continental intraplate volcanism. The oceanic sector constitutes a mildly alkaline volcanic series, which evolves towards phonolite, while the continental sector evolves towards rhyolite (e.g., Fitton, 1980). Isotopic studies of lavas (Halliday et al., 1988) divide the CVL into three sectors: an oceanic zone, ocean-continent boundary zone and a continental zone.

The study area overlaps two (coastal and tropical western highlands) of the five climatic zones in Cameroon, with mean annual rainfall of 5000 and 3000 mm, mean annual atmospheric

temperatures of 26°C and 21°C, humidity of 85% and 80%, and evaporation of 600 mm and 700 mm, respectively (Sighomnou, 2004). Hydrologically, three (coastal, Sanaga, and Niger) of the five river basins in Cameroon drain the study area in a dendritic manner. According to Le Marechal (1968) and Tanyileke (1994), riverine and in aquifer waters encounter heat and mantle-derived CO_2 gas that emanate through the CASZ, causing heating and bubbling of the spring systems along the CVL. At each spring site the gas phase manifests as either bubbles or 'rotten egg' smell, while the precipitates occur as white films, white grains in volcanic ash, stalactite and stalactmite in caves, and mounds around orifices as shown in Fig. 3. At the sites of Sabga A in Fig. 3, animals consume the water as a source of salt, while humans exploit the precipitates for food recipes.

Method of study

Water and precipitate samples were collected from selected bubbling soda spring sites along the CVL (Fig. 3) in October 2015. Each water sample was collected in 3 acid-washed 250 ml polyethylene bottles after rinsing them thrice with the sample. At each sampling site, an unfiltered, unacidified and tightly corked sample was collected in one bottle for subsequent analyses for stable environmental isotopes of hydrogen (δ^2H) and oxygen ($\delta^{18}O$). The second bottle contained un-acidified but filtered sample for anion analyses, and the third filtered and acidified sample for cations and trace elements analyses. Prior to sample collection, in-situ physicochemical measurements were recorded for pH (TOA-DKK HM-30P meter), electrical conductivity (TOA-DKK CM-31P EC meter), reduction-oxidation potential (TOA-DKK ORP meter), and water temperature. Geographical parameters (latitude, longitude and altitude) of each sample site were recorded in the field using a hand-held Garmin GPS. Alkalinity was measured using a ''Hach'' field titration kit, after addition of 0.16 N H_2SO_4 to the sample to reach the endpoint titration (pH 4.5). Samples were filtered through 0.2 μm filters prior to major ions and dissolved silica determination. Three kilograms chunks of massive carbonate was chipped off with a hammer at sites with consolidated precipitate, and 300 g scoped from sites with unconsolidated precipitate. Each precipitate was put in a clean plastic container, sealed and labelled.

Water samples and precipitates were transported to the University of Toyama, in Japan for chemical analyses.

The various chemical analyses that were done in various institutes in Japan are tabulated in Table 1.

Results and Discussions

Variation of water chemistry

Chemical compositions and isotopic ratios of water samples and carbonate phases are presented in Tables 2 and 3. Measured in-situ parameters show values in the range of 54 - 13130 µS/cm for EC, 4.3 - 7.5 for pH, and 19.3 - 47.4°C for water temperature.

The chemistry of the observed water resources determined with the use of the Piper's diagram (Piper, 1944) (Fig. 4a), shows that water from the Lobe soda springs and its nearby hand dug wells, located in the ocean-continent-boundary (OCB) and close to the ocean (Fig. 4a), have a dominant Na+K-Cl signature. On the other hand, water from the soda springs in Sabga, Bambui, and Nyos have dominantly Ca+Mg-HCO_3 signature. The observed disparity in water facies may be due to the proximity of the Lobe springs to the ocean, which impacts the sodium chloride characteristics as accorded in Le Marechal (1976). Whilst in the other springs, an interaction between primary and secondary minerals in rocks and water could be the dominant explanation as also explained by other researchers (Kamctueng et al., 2014; Fantong et al., 2015). The Stiff diagrams for the water chemistry (Fig. 4b), also depict similar water facies like the Piper's diagram, but they further suggest varying degree of mineralization of the water sources. In the OCB, the larger sizes of the stiff diagram for the Lobe soda springs indicate more mineralization than for water from the wells. Likewise in the samples from the continental sector (CS) the water in the Sabga soda springs are most mineralized, followed by those in Bambui and the least mineralized is that from the Nyos soda spring. The observed variation in degree of mineralisation could in part be indicating variation in residence time, where the older springs are enriched in elements from aquifer minerals than in younger springs (e.g., Fantong et al., 2010a; Kamctueng et al., 2015) that are renewed through a local and short recharge-discharge flow paths.

Recharge mechanisms and evaporation of the sampled waters

Isotopic ratios of hydrogen and oxygen, which are used in this study to infer recharge and evaporation mechanisms in the waters are also shown in Table 2 and graphically presented in Fig. 5. The δD values ranged from -41.8 in Sabga A soda spring to -26 ‰ in water from well 5.

Oxygen isotope ($\delta^{18}O$) values range from -6.3 ‰ in Sabga A spring to -3.1 ‰ in water from well 3. Due to the paucity of isotope data on local rainfall, the Global Meteoric Water Line (GMWL) of Craig (1961), which is defined by the line $\delta D = 8\delta^{18}O + 10$ is also presented as a reference. Distribution of sample water in the δD-$\delta^{18}O$ graph suggests that water in the Bambui and Sabga soda springs are subject to little or no evaporation, while the Lobe soda springs suggest slight evaporation, but water from the wells and Nyos soda springs show remarkable evaporation tendencies. Such a pattern depicts that the Bambui and Sabga soda springs are subject to the mechanism of preferential flow pass, which is caused by rapid recharge (e.g., Tsujimura et al., 2007; Asai et al., 2009), that is favored by the highly altered and jointed lavas as opposed to the Lobe and Nyos cave soda springs, and the wells. Except for the Lobe soda springs, the other springs are sources of drinking water for animals (cattle and goats), and a source of minerals (carbonate) for local manufacture of soup for consumption by the nearby population, thus it is important to assess at a preliminary scale the medical hydrogeochemical characteristics of the springs.

Health implications of the water chemistry

Given that the gas bubbling springs are located in the area of livestock rearing and human activities, their chemistry is here preliminarily evaluated to assess potential health implications. With respect to fluoride, Figure 6a shows that except for the Nyos cave soda spring, all the other soda springs contain fluoride at concentrations that are above the WHO optimal limit (1.5 mg/l e.g., Kut et al., 2016). This indicates that the animals and the population that exploit these springs are potentially exposed to fluoride poisoning as reported by Fantong et al. (2010b) in the Far Northern Region of Cameroon. The potential geogenic and volcanic provenance (Davies, 2013), and actual epidemic effects of such high concentrations of fluoride are not within the scope of this study, and need further investigation.

With respect to arsenic (As), Figure 6b shows that the Sabga soda springs contain As at concentrations as high as 1.33 ppm that are above the WHO upper limit (0.03 ppm in drinking water). Based on the field observations that water from the Sabga soda springs is heavily consumed by cattle, and carbonate there-from is exploited for consumption by the population, it is also a challenge for medical geochemists to carry out a comprehensive investigation into the incidence, origin, mobilization and epidiomological effects of arsenic in these areas.

Impact of volcanic volatile or magmatic input on chemistry of the spring water

The dissolved state of elements and saturation state of compounds observed in the springs are to an extent determined by their saturation indices and stoichiometry (e.g., Faure, 1991).

Saturation indices and activity diagrams

The saturation index (SI) of a given mineral in an aqueous system is defined as (Lloyd and Heathcoat, 1985; and Deutch, 1997):

$$\mathrm{SI} = \log\left(\frac{\mathrm{IAP}}{\mathrm{K_{sp}}}\right) \qquad (1)$$

where IAP is the ion activity product and K_{sp} is the solubility product of the mineral in the system. A SI > 0 points to supersaturation, and a tendency for the mineral to precipitate from the water. Saturation can be produced by factors like incongruent dissolution, common ion effect, evaporation, and rapid increase in temperature and CO_2 exsolution (Appelo and Postma, 2005). A SI < 0 points toward undersaturation, and implies that water dissolves the minerals from surrounding rocks. Negative SI value might also reflect that the character of water is either from a formation with insufficient concentrations of the mineral for precipitation to occur (Garrels and Mackenzie, 1967).

The thermodynamic data used in this computation are those contained in the database of 'Phreeqc for Windows'. A plot of the calculated SI (with respect to quartz, anhydrite, aragonite, calcite and dolomite) versus TDS (Fig.7) groups the water samples into three subgroups: subgroup 1, which consists of water from the shallow wells is undersaturated with respect to all the selected phases and has the lowest TDS values that ranged from 63-83 mg/l. The undersaturation of subgroup 1 suggests that no mineral precipitates in the wells as observed on the field. Subgroup 2, which consists of Nyos cave soda spring, Bambui soda spring B and Sabga soda spring B, show supersaturation with respect to quartz, dolomite. On the field, this subgroup is found to be dominantly precipitating trona (a Na-rich carbonate) and dolomite to a lesser extent. Subgroup 3 that consists of the Lobe and Sabga A soda springs, are supersaturated with respect to dolomite, quartz and calcite, and it is actually precipitating more of dolomite, and trona to a lesser extent.

The stability of secondary minerals (Na and Ca montmorillonites, kaolinite, gibbsite) and amorphous quartz in the springs and wells were evaluated by plotting log (a_{Na}/a_{H}) vs log (a_{H4SiO4})

(the albite system) (Fig. 8a) and log (a $_{Ca2}$/a$_{2H}$) versus log (a$_{H4SiO4}$) (the anorthite system) (Fig. 8b). These diagrams were drawn with the assumption that aluminum was preserved in the weathering product (Appelo and Postma,1993), because the amount of alumina will remain constant in fresh rocks and its altered equivalent. The constant amount in alumina (Al_2O_3) is because an apparent increase in its weight % is actually always caused by a reduction in the weight of the fresh rock to some smaller amount (Faure, 1991). End member compositions were also assumed using equilibrium relationship for standard temperature (25°C) and pressure (1 atmosphere), which approximately reflect the springs and groundwater conditions. Activities of the species were computed using the analytical concentrations and activity coefficient determined by Phreeqc for Windows version 2.1 under the above conditions (Appelo and Postma, 1993). According to the figures, groundwater from the wells span the stability field of kaolinite, while all the soda springs with exception of the Nyos soda spring are in equilibrium within the Na and Ca -montmorillonite stability fields. This concurs with the incidence of clay minerals in the study area (Fantong et al., 2015). Moreover, the presence of kaolinite and montmorillonite in the study area occur as groundmass in the XRD (X-Ray Defraction) peaks of Figures 9b,10b, 11b, 12b, and 14b. A combination of information from the saturation indices and stability diagrams is supported by the presence of precipitating carbonate phases in the soda springs as shown in Fig. 1.

Typology of carbonate phases

The typology of the carbonate phases that precipitate from the observed soda springs is done by describing the morphology by using SEM images, and identifying the carbonate phase by using XRD diagrams and EPMA elemental mapping.

Carbonate from the Nyos cave soda spring

The SEM image in Fig. 9a shows that the carbonate is an association of cluster of powdery amorphous groundmass upon which sub-euhedral crystals developed. This carbonate is identified with XRD peaks (Fig.9b) as a trona (low- syn trisodium hydrogen dehydrate carbonate). To accentuate the trona phase, an elemental EPMA mapping (Fig.9 c, d, e and f) shows the dominance of sodium, traces of calcium and total absence of magnesium.

Carbonate from Sabga A soda spring

The SEM image of Fig. 10a shows that the carbonate is nail-shaped stalactite crystals protruding from a cluster of powdery amorphous groundmass. This carbonate is identified with XRD peaks (Fig.10b) as a dolomite (calcium-magnesium bicarbonate). Dolomite precipitate in this spring is supported by an elemental EPMA mapping (Fig. 10 c, d, e and f), which shows a dominance and remarkable presence of both calcium and magnesium, with traces of sodium.

Carbonate from Sabga B soda spring

The SEM image of Fig. 11a shows that the carbonate is made up of radiating tabular columns of crystals whose faces are edged by bacteria. This carbonate is identified with XRD peaks (Fig. 11b) as a trona (low-syn trisodium hydrogen dehydrate carbonate). The presence of this trona precipitating in this spring is justified by an elemental EPMA mapping (Fig. 11c, d, e and f), which shows a dominance of sodium and an almost absence of calcium and magnesium.

Carbonate from Bambui B soda spring

The SEM image of Fig. 12a shows that the morphology of the carbonate is an intersecting mosaic of tabular crystals whose faces are edged by bacteria. This carbonate is identified with XRD peaks (Fig. 12b) as a trona similar to that of Sabga B. The presence of this trona precipitating in this spring is supported by an elemental EPMA mapping (Fig. 12 c, d, e and f), which shows a dominance of sodium and low content of calcium and magnesium. The disseminated distribution of fluorine, which almost coincide with the distribution of faint calcite suggest the presence of fluorite (CaF), which could be dissolving to enrich the water phase with fluoride as seen in Fig. 13e.

Carbonate from Lobe D soda spring

The SEM image of Fig. 14a shows that the carbonate is a coliform flower-shape radiating crystals, which is colonized by bacteria. This carbonate is identified with XRD peaks (Fig. 14b) as a dolomite. The occurrence of dolomite as the precipitate in this spring is supported by an elemental EPMA mapping (Fig. 14c, d, e and f), which shows high content of both calcium and magnesium, and low content of sodium.

Summarily, the carbonate phases that are precipitating from the studied soda springs along the CVL are dominantly dolomite and trona. The pristine geochemical attributes and characteristics of the carbonate are at a later phase altered (Demeny, 2016) by diatoms and bacteria as shown in Figure 11a and 12a. The incidence of bacteria in such a hydrogeochemical system leaves biogeochemists with another opportunity to assess the incidence and role of bacteria in the soda spring systems.

Origin of the fluids and carbonates

In a bid to identify the formation (sources and paleo temperature) processes that led to the formation of the observed carbonates, we used ^{13}C isotopes, ^{87}Sr/^{86}Sr, carbonate-water fractionation temperatures, and Cl^- versus F^- plot as geochemical tracers.

Carbonate-water fractionation temperature

Although oxygen-isotope thermometry based on isotopic fractionation of oxygen between carbonates and water dates back to the Mid-1900s, the carbonate-water oxygen isotopic fractionation equations are still being discussed. The use of isotope thermometry is based on several criteria: (i) the temperature dependence of the isotopic fractionation between the investigated compounds (in our case dolomite/trona and water) and (ii) the isotopic compositions of the compounds are known, (iii) the isotopic equilibrium between the compounds can be proven or at least reasonably assumed, and (iv) no subsequent isotopic alteration occurred after the deposition of carbonates. These considerations are valid for inorganic carbonate formation, as biogenic carbonate is severely affected by the organisms' metabolism, resulting in a species-dependent ''vital effect'' (Demeny et al., 2010 and references therein)

The temperatures at which the carbonate phases precipitate from the springs were calculated by using the empirical equation for the temperature dependence of calcite-water oxygen isotope fractionation from 10 to 70 °C as shown in equations 2 and 3 that were reported by Demeny et al. (2010).

$1000.\ln\alpha = 17599/T - 29.64$ [for travertines with a temperature range of 30 to 70^{o}C] (2)

$1000.\ln\alpha = 17500/T - 29.89$ [for cave deposits for the range 10 to 25^{o}C] (3)

The variable T are in ^{o}C.

The values obtained suggest that carbonates precipitate from soda springs along the CVL at temperature that varied from 18.5 - 43°C. The lowest fractionation temperatures (18.5 - 18.6°C) occurred in the Sabga soda springs, while the highest (35 - 43°C), occurred in the Lobe soda springs (Table 3). A plot (Fig. 15), shows that with the exception of the dolomite in the 'Sabga A soda spring', the tronas fractionated at lower temperature (~18.5 - 20 °C) than the dolomites, which fractionated at temperature ranging from 35.2 - 43°C. Based on Figure 15, the oxygen isotopes in carbonates precipitating along the Cameroon Volcanic Line yielded an empirical fractionation– temperature equations of:

$$1000.\ln\alpha = -0.2153T + 35.3 \qquad (4)$$

Stable isotopes of ^{13}C, $^{87}Sr/^{86}Sr$, and ^{18}O

The observed carbonates (dolomite and trona) facies in the samples showed broad ranges in ^{87}Sr/^{86}Sr, ^{13}C and δ^{18}O. The ^{87}Sr/^{86}Sr ratio varied from 0.706 - 0.713, the ^{13}C varied from -3.09 to 5.22 VPDB and δ^{18}O from -8.4 to -1.4 VPDB as shown in Table 3. Their δ^{13}C values of observed dolomites are close to the range of values reported for carbonates precipitating from seawater (0 -4 VPDB; Veizer et al., 1999; Shah et al., 2012). Indication of marine origin of the dolomites corroborates with field observation, because the dolomite precipitates from the Lobe soda spring located in the OCB of the study area. However, the carbonates (trona) identified in our study area showed relatively depleted δ^{13}C signatures, which may indicate a possible external source of carbon during trona precipitation (Fig. 16) or a temperature dependent fractionation effect (Shah et al., 2012). The depleted δ^{18}O in dolomite from the 49°C Lobe soda springs, may be due to its higher temperatures (thermogenic type) (Bisse et al., 2018), given that precipitation of dolomite from hot springs leads to relatively depleted δ^{18}O ratios (Land, 1983).

With exception of the Lobe soda springs, where ^{87}Sr/^{86}Sr value did not vary between the carbonate and water phases, in the other soda springs (Bambui soda springs A and B, Sabga soda springs A and B, and Nyos cave soda spring), the ^{87}Sr/^{86}Sr ratio shows a decoupling tendency where the water phases contain relatively higher values than the carbonate phases (Fig. 17a). The relatively higher ^{87}Sr/^{86}Sr ratio in the Lobe soda springs may indicate interaction of dolomitizing fluids with radiogenic lithologies (Shah et al., 2012), which commonly occur along the CVL (e.g., Aka et al., 2000; 2001). Moreover, the ^{87}Sr/^{86}Sr versus ^{18}O cross plot (Fig. 17b), shows that the dolomites are richer in ^{87}Sr/^{86}Sr ratio than the tronas. However, the signatures in the dolomite

of the Sabga soda spring “A” together with those in the tronas are closer to those of the marine signatures (McArthur et al., 2001). Such marine signatures in tronas (Na-rich carbonate) within the continental sector of the Cameroon Volcanic Line, may suggest the presence of paleo-continental sabkha environments, where various sodium carbonates have been recorded in tropical regions (Whitten and Brooks, 1972). This suggestion, however, requires further investigation.

Implications for monitoring and hazard mitigation

Volcanogenic sources of fluorine (e.g., Symonds et al., 1987; Symonds et al., 1988; Bellomo et al., 2003) and chlorine (e.g., Keene and Graedel 1995) containing gasses have been reported in active and passive volcanic areas, and recently in the Nyiragongo volcano in Congo (Liotta et al., 2017). As used by the later, we also used a cross plot of chloride versus fluoride (Fig. 18) to infer volcanogenic contribution in the observed springs along the CVL. The figure suggests volcanogenic inputs into the Lobe, Nyos, Sabga A, and Bambui A springs. The implication of a volcanic input to these fluids suggests that they can be used to monitor volcanic activity and thus mitigate hazards, especially in the vicinity of the Lobe spring located close to the currently active Mt. Cameroon. Moreover, the dominant fluids in the Lobe, Nyos, Sabga A, and Bambui A springs are magmatic CO_2 and H_2O (Sano 1990). Water dissolves slightly more in silicic melts than in basaltic melts, whereas CO_2 dissolves more in basaltic than in silicic melts. Kusakabe (2017) reports that the solubility of CO_2 and H_2O in basaltic melts at 1200°C is a function of the total pressure of the volatiles, whose composition in the melt changes as the decompression proceeds. For example, at low pressure the mole fraction of H_2O equals 0.2 and that of CO_2 is 0.8, implying that basaltic melt becomes rich in CO_2 as the magma ascends and the confining pressure reduces, resulting to degassing. If degassing takes place in an open system, CO_2-rich fluid leaves the magma. This solubility-controlled behavior of CO_2 in basaltic magma may explain a CO_2-rich nature of fluids separated from the magma. The ultimate source of CO_2 in the Nyos, Lobe, Sabga A, and Bambui A springs may therefore be derived from the decarbonation of crystallized metasomatic fluids in the subcontinental lithosphere (Aka, 2015; Asaah et al., 2015). The low (-2 to -3 ‰) ^{13}C values of carbonates in the Nyos and Sabga soda spring may also indicate magmatic origin of the CO_2 that contributes in precipitating the carbonates. Thus, the

permanent supply of such CO_2 in the springs provides good sites for monitoring volcanic activity for hazard mitigation.

Conclusions

The chemistry of water in the bubbling soda springs observed along the Cameroon Volcanic Line shows an evaporated Na+K-Cl and non-evaporated Ca+Mg-HCO_3 facies in the ocean continental boundary sector (OCB) and continental sector (CS), respectively. In the OCB, the Lobe soda springs shows more mineralization than water from nearby hand dug wells. This may indicate that spring water (T=49°C) is circulating deeper than the well water. In the continental sector (CS) the water in the Sabga soda springs are the most mineralized, followed by those in Bambui soda spring and the least mineralized is the Nyos soda spring. With exception of the soda springs in the Nyos area, all other studied soda springs contain fluoride from geogenic fluorine at concentrations above the WHO upper limit, whilst concentrations of arsenic (> 0.3 mg/l) that also call for health concern occur in the Sabga soda springs. The observed soda springs are either saturated or super-saturated with respect to quartz, and carbonate phases, which are actually precipitating as dolomite and trona. The carbonate-water fractionation temperature varies from 18.5 - 43°C. X-ray diffraction spectra and chemical mapping by electron probe microanalyzer unraveled that the precipitating carbonates occur as dolomite in the Lobe and Sabga A soda springs, and as trona in the Nyos, Bambui and Sabga B soda springs. Scanning electron microscope (SEM), reveals various morphologies of the carbonates, including amorphous to tabular euhedral tronas, and nail shaped to bacteria-colonized coliform dolomites. Geochemical tracers of ^{13}C, $^{87}Sr/^{86}Sr$, and ^{18}O indicate a dominantly marine provenance of the carbonate. Chloride versus fluoride cross plot suggest a contribution from volcanic volatiles in the Lobe, Nyos, Sabga A, and Bambui A springs. This contribution of a volcanic input to these fluids suggests that they can be used to monitor volcanic activity and thus mitigate hazards, especially in the vicinity of the Lobe spring that is located close to the currently active Mt. Cameroon.

Acknowledgements

We thank the Institute of Geological and Mining Research (IRGM), Yaoundé, for financial and logistical support during sampling. Thanks to the funders (JICA and JST) of SATREPS-IRGM project that provided field and laboratory equipment that were used to generate the data during

this study. We thank all the members of the Department of Environmental Biology and Chemistry, University of Toyama, Japan, for their enriching comments during the preparation of this manuscript. We are also grateful to Prof. Suh Emmanuel and Prof. Loic Peiffer for their review comments that enriched the content of the manuscript.

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Figures captions

Fig. 1. Locations of sampled carbonate depositing soda springs along the Cameroon Volcanic Line (CVL). CS stands for the continental sector of the CVL, and OCB stands for the oceanic continental boundary of the CVL. The locations of Lake Monoun (L. Monoun), Lake Nyos (L. Nyos), and Mount Cameroon (Mt. Cameroon) are also shown. The black dots correspond to samples' locations

Fig.2. Herds of cattle consuming water from the carbonate depositing springs that have been harnessed

Fig. 3. Samples (deposited carbonates and water) collection sites from observed springs

Fig. 4. Water chemistry presented as Piper's diagram (a), and Stiff diagrams (b) for the observed springs

Fig. 5. Plot of δH and $\delta^{18}O$ in water from observed springs. The Sabga and Bambui springs showed no evaporation effect, while the Lobe springs, the Nyos spring and water in shallow wells around Lobe spring were subjected to evaporation relative to the meteoric water lines. Zone 1 represents the soda springs and zone 2 represents shallow groundwater in the Lobe spring neighborhood. LMWL: Local meteoric water line. GMWL: Global meteoric water line

Fig. 6. With respect to fluoride concentrations (a), all the observed soda springs with exception of that in Nyos, contain fluoride above the WHO upper limit of 1.5 mg/l. With respect to Arsenic (As) concntrations (b), the springs in the continental sector contain As above the WHO upper limit

Fig. 7. The plots of saturation indices (SI; with respect to quartz, anhydrite, aragonite, calcite and dolomite) versus total dissolved solid (TDS) for investigated water samples (wells and springs), show three subgroups (1: undersaturated wells. 2: trona precipitating springs. 3: dolomite precipitating springs).

Fig. 8. Stability diagrams for some minerals in the systems Na_2–Al_2O_3–SiO_2–H_2O (a) and CaO–Al_2O_3–SiO_2–H_2O (b) at 25°C

Fig. 9. The scanning electron microscope image (a), X-ray diffraction peaks (b), and electron probe microanalyzer mapping (c,d, e,f) of carbonate precipitate from Nyos cave spring

Fig. 10. The scanning electron microscope image (a), X-ray diffraction peaks (b), and electron probe microanalyzer mapping (c,d, e,f) of carbonate precipitate from the Sabga A spring

Fig. 11. The scanning electron microscope image (a), X-ray diffraction peaks (b), and electron probe microanalyzer mapping (c,d, e,f) of carbonate precipitate from the Sabga B spring

Fig.12. The scanning electron microscope image (a), X-ray diffraction peaks (b), and electron probe microanalyzer mapping (c,d, e,f) of carbonate precipitate from Bambui B spring

Fig. 13. Electron probe microanalyzer mapping of Na, Ca, Mg, and F of carbonate precipitate from Bambui B spring, showing enrichment of fluorine in the matrix of the carbonate

Fig. 14. The scanning electron microscope image (a), X-ray diffraction peaks (b), and electron probe microanalyzer mapping (c,d, e,f) of carbonate precipitate from Lobe D spring

Fig. 15. Carbonates-water oxygen isotopic fractionation temperature in observed soda springs along the CVL. Dolomites fractionated at relatively higher temperatures (35-43°C) than tronas (circum 20°C).

Fig. 16. Plots of ^{13}C and δ^{18}O (PDB), showed observed tronas to be relatively depleted in ^{13} C and enriched in ^{18}O (PDB).

Fig. 17. Except for the Lobe springs that showed highest $^{87}Sr/^{86}Sr$ ratio, in all the other observed springs the carbonate phases are relatively enriched in $^{87}Sr/^{86}Sr$ ratio than the water phase (a), and $^{87}Sr/^{86}Sr$ are relatively depleted in tronas than in dolomites (b)

Fig. 18. Chloride versus fluoride cross plots showing volcanogenic contributions into the Lobe, Bambui and Nyos springs

Table captions

Table 1. Laboratory analytical methods of the carbonates and water phases in observed springs

Table 2. Chemical composition of water from the observed springs and shallow wells. ND: not detected. NM: not measured

Table 3. Fractionation temperature and isotopic compositions of carbonates precipitating from the observed springs

Table 3.

Sample name	δ^{18}O (SMOW) carbonate	δ^{18}O (SMOW) water	1000lnα (δ^{18}O calcite-water)	Fractionation temperature (°C)	Observed temperature (°C)	^{13}C carbonate (VPDB)	^{18}O carbonate (VPDB)	^{87}Sr/^{86}Sr in carbonate	Carbonate type
LobeD ssp	22.17	-4.65	26.82	43	49	1.74	-8.44	0.713	Dolomite
Lobe Assp	22.68	-4.70	27.38	35.2	47.4	5.22	-7.1	0.713	Dolomite
Bambui B ssp	24.92	-6.30	31.22	20	22.2	-1.84		0.707	Trona
Bambui A ssp	25.2	-6.7	31.90	19.8	21.8			0.707	Trona
Sabga B ssp	25.00	-6.30	31.30	18.6	19.3	-1.98	-1.4	0.707	Trona
Sabga A ssp	24.23	-6.01	31.09	18.5	20	-3.09	-5.6	0.708	Dolomite
Nyos C ssp	24.92	-3.40	28.32			-2.1	-5.9	0.706	Trona

SMOW : Standard Mean Ocean Water. VPDB : Vienna Pee Dee Belemnite. °C : Degree Celsius. Ssp :Soda springs. Chemical formula for dolomite is $CaMg(CO_3)_2$ and for trona is $Na_3H(CO_3)_2.H_2O$

Table 1

Table 1: Summary of laboratory analytical procedures during the studies

Mineral phase	**Parameter analyzed/determined**	**Equipment used**	**Analytical precision/data reliability and conditions**	**Institution**
Carbonate	Crystal habit	Scanning Electron Microscope, TM-1000 miniscope	Vacc : 15.0kV Accelerating voltage : 15000V Emission current : 102.6mA Sample coating : Gold	University of Toyama, Japan
	Carbonate type	X-Ray Diffraction (XRD). Bruker model D8 Discover-TUS, serial No 27062	Voltage : 30kv Current : 15mA Scan speed 4000°/minute Measurement angle : 3-60°	University of Toyama, Japan
	Elemental composition	JEOL, JXA-8230T Electron Probe Micro Analyzer (EMPA)	Voltage : 15kv Current : 1.001-9e-0008A Time (ms) : 2.00	University of Toyama, Japan
	$^{87}Sr/^{86}Sr$	Thermal Ionization Mass Spectrometer (TIMS)	2σ = ±2E-5	Research Institute for Humanity and Nature- Kyoto
	^{13}C and ^{18}O	Isotope Ratio Mass Spectrometer (IRMS), after decomposing carbonate with 100% phosphoric acid	±0.1‰	University of Toyama, Japan

		at 25°C (McCrea, 1950)		
Water	Major cations and anions	Alkalinity titration for HCO_3^-, and Ion chromatography for the other ions. More details are explained in Fantong et al. 2008; 2010; and 2016	±10 %	University of Toyama, Japan
	Stable Environmental Isotopes (^{2}H and ^{18}O)	Micromass model prism Isotope Ratio Mass Spectrometer, as explained in Coleman et al. 1982 for ^{2}H, and Epstein and Mayeda 1953 for ^{18}O	±1.5 ‰ for δD and ±0.1‰ for δ^{18}O	University of Toyama, Japan
	Trace elements including arsenic	ICP-MS	SD = ±0.5	University of Toyama, Japan

Major ions, $\delta^{18}O$, $\delta^{13}C$ and $^{87}Sr/^{86}Sr$ compositions of water and precipitates from springs along the Cameroon Volcanic Line (Cameroon, West Africa): Implications for provenance and volcanic hazards

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Abstract

A combined study of major ions, $\delta^{18}O$, δD, ^{13}C, $^{87}Sr/^{86}Sr$ isotopes, X-ray diffraction, scanning electron microscopy, and electron probe microanalyses on springs and spring mineral precipitates along the Cameroon Volcanic Line (CVL) was undertaken to understand water chemistry, and infer the type and origin of the precipitates. The waters are of evaporated Na+K-Cl and non-evaporated Ca+Mg-HCO_3 types, with the more mineralized (electrical conductivity-EC of 13130 μS/cm) Lobe spring inferred to result from interaction of circulating 49°C waters with magmatic volatiles of the active Mt. Cameroon. Water mineralization in the other springs follows the order: Sabga A > Sabga B> Bambui B > Bambui A > Nyos Cave. But for the Nyos Cave spring, all other springs contain fluoride (up to 0.5 - 35.6 mg/l above WHO potable water upper limit). The Sabga spring contains arsenic (up to 1.3 mg/l above the WHO limits). The springs show low fractionation temperatures in the range of 19 – 43 °C. The Lobe and Sabga A springs are precipitating dolomite ($CaMg(CO_3)_2$), while the Nyos Cave, Bambui A, Bambui B

and Sabga B springs precipitate trona ($(Na_3H(CO_3)_2.H_2O)$). Our data suggest a marine provenance for the carbonates, and point to a volcanic input for the Lobe, Nyos, Sabga A, and Bambui A springs. The latter springs are therefore proposed as proxies for monitoring volcanic activity for hazard mitigation along the CVL.

Key words: *Bubbling springs. Precipitates. Composition. Provenance. Volcanic activity. Hazards mitigation.*

Introduction

Mineral-depositing springs are natural systems that offer a good opportunity to study various mechanisms by which waters establish equilibrium with conditions at the Earth's surface (Amundson and Kelly, 1987; Omelon et al., 2006). For example, carbonate-precipitating waters provide an opportunity to evaluate a dynamic carbonate system and the major controls associated with calcite precipitation (Barnes, 1965; Jacobson and Usdowski, 1975), including; isotope fractionation associated with natural calcite precipitation from spring waters (McCrea, 1950; Friedman, 1970; Usdowski et al., 1979; Dandurand et al., 1982; Amundson and Kelly,1987; Usdowski and Hoefs, 1990; Hamilton et al.,1991; Liu et al., 2003), as well as the types, morphologies, textures, and processes involved in the formation of various carbonate phases (Tucker and Bathurst, 1990; Bradley and Eugster, 1969; Ford and Pedley, 1996; Forti, 2005).

Many orifices of gas-water-carbonate interacting systems occur along the Cameroon Volcanic Line (CVL-Fig. 1). Based on carbonate enrichment studies on volcanic debris and springs in part of the continental sector of the CVL (Le Marechal, 1976; Verla et al., 2014); chemical and isotopic characteristics of fluids along the CVL (Tanyileke , 1994); the geochemistry of gases in springs around Mt. Cameroon and Lake Nyos (Kusakabe et al., 1989; Sano et al.,1990; Aka, 1991); the sedimentology and geochemistry of the Bongongo and Ngol travertines along the CVL (Bisse et al., 2018), the following hypotheses have been proposed: (1) the bubbling mineral springs along the CVL contain abundant CO_2. (2) The CO_2 in the bubbling springs is dominantly of magmatic origin. (3) Helium and carbon isotope ratios of gases from a few of the springs

along the CVL revealed a signature similar to hotspot type magma. (4) The precipitating minerals are travertines.

Although these studies provide initial data to understand the geochemical dynamics within the CVL gas-water-carbonate systems, gaps required to better understand the system include; a) a total absence of comprehensive information on the classification and genetic processes of the precipitating carbonates, which is exploited by the indigenes for preparation of traditional soup, b) high concentration (> 100 mg/l) of geogenic fluoride has been reported (e.g., Kut et al., 2016; and references there-in) in thermal waters along the Ethopian rift. Such concentrations of fluoride in water that is used for domestic purposes and livestock rearing can cause tremendous health effects (e.g., Fantong et al., 2010). Livestock rearing on the slopes of the CVL heavily consumes water from the springs (Fig. 2), so there is still a need to re-assess their chemical characteristics with focus on potential harmful elements like fluoride and arsenic, and c) the carbonate-water fractionation temperature remains unknown.

Against this backdrop, the objectives of this study are to 1) characterize the water chemistry with focus on health implications, 2) estimate the carbonate-water fractionation temperature, and 3) identify, describe and classify the carbonates that are precipitating from the springs.

Study area

Figure 1 shows, the sample sites along the CVL, a prominent 1600 km long Y-shaped chain of Tertiary to Recent, generally alkaline volcanoes that overlap an array of dextral faults called the Central Africa Shear Zone (CASZ) (Ngako et al., 2006) on the African continent, comparable only to the East Africa Rift System. The CVL follows a trend of crustal weakness that stretches from the Atlantic Island of Annobon, through the Gulf of Guinea, to the interior of the African continent (Fitton, 1980; Déruelle et al., 1987, Halliday et al., 1988;). It is unique amongst intraplate volcanic provinces in that it straddles the continental margin and includes both oceanic and continental intraplate volcanism. The oceanic sector constitutes a mildly alkaline volcanic series, which evolves towards phonolite, while the continental sector evolves towards rhyolite (e.g., Fitton, 1980). Isotopic studies of lavas (Halliday et al., 1988) divide the CVL into three sectors: an oceanic zone, ocean-continent boundary zone and a continental zone.

The study area overlaps two (coastal and tropical western highlands) of the five climatic zones in Cameroon, with mean annual rainfall of 5000 and 3000 mm, mean annual atmospheric

temperatures of 26°C and 21°C, humidity of 85% and 80%, and evaporation of 600 mm and 700 mm, respectively (Sighomnou, 2004). Hydrologically, three (coastal, Sanaga, and Niger) of the five river basins in Cameroon drain the study area in a dendritic manner. According to Le Marechal (1968) and Tanyileke (1994), riverine and in aquifer waters encounter heat and mantle-derived CO_2 gas that emanate through the CASZ, causing heating and bubbling of the spring systems along the CVL. At each spring site the gas phase manifests as either bubbles or ‘rotten egg’ smell, while the precipitates occur as white films, white grains in volcanic ash, stalactite and stalactmite in caves, and mounds around orifices as shown in Fig. 3. At the sites of Sabga A in Fig. 3, animals consume the water as a source of salt, while humans exploit the precipitates for food recipes.

Method of study

Water and precipitate samples were collected from selected bubbling soda spring sites along the CVL (Fig. 3) in October 2015. Each water sample was collected in 3 acid-washed 250 ml polyethylene bottles after rinsing them thrice with the sample. At each sampling site, an unfiltered, unacidified and tightly corked sample was collected in one bottle for subsequent analyses for stable environmental isotopes of hydrogen (δ^2H) and oxygen ($\delta^{18}O$). The second bottle contained un-acidified but filtered sample for anion analyses, and the third filtered and acidified sample for cations and trace elements analyses. Prior to sample collection, in-situ physicochemical measurements were recorded for pH (TOA-DKK HM-30P meter), electrical conductivity (TOA-DKK CM-31P EC meter), reduction-oxidation potential (TOA-DKK ORP meter), and water temperature. Geographical parameters (latitude, longitude and altitude) of each sample site were recorded in the field using a hand-held Garmin GPS. Alkalinity was measured using a ‘‘Hach’’ field titration kit, after addition of 0.16 N H_2SO_4 to the sample to reach the endpoint titration (pH 4.5). Samples were filtered through 0.2 μm filters prior to major ions and dissolved silica determination. Three kilograms chunks of massive carbonate was chipped off with a hammer at sites with consolidated precipitate, and 300 g scoped from sites with unconsolidated precipitate. Each precipitate was put in a clean plastic container, sealed and labelled.

Water samples and precipitates were transported to the University of Toyama, in Japan for chemical analyses.

The various chemical analyses that were done in various institutes in Japan are tabulated in Table 1.

Results and Discussions

Variation of water chemistry

Chemical compositions and isotopic ratios of water samples and carbonate phases are presented in Tables 2 and 3. Measured in-situ parameters show values in the range of 54 - 13130 µS/cm for EC, 4.3 - 7.5 for pH, and 19.3 - 47.4°C for water temperature.

The chemistry of the observed water resources determined with the use of the Piper's diagram (Piper, 1944) (Fig. 4a), shows that water from the Lobe soda springs and its nearby hand dug wells, located in the ocean-continent-boundary (OCB) and close to the ocean (Fig. 4a), have a dominant Na+K-Cl signature. On the other hand, water from the soda springs in Sabga, Bambui, and Nyos have dominantly Ca+Mg-HCO_3 signature. The observed disparity in water facies may be due to the proximity of the Lobe springs to the ocean, which impacts the sodium chloride characteristics as accorded in Le Marechal (1976). Whilst in the other springs, an interaction between primary and secondary minerals in rocks and water could be the dominant explanation as also explained by other researchers (Kamctueng et al., 2014; Fantong et al., 2015). The Stiff diagrams for the water chemistry (Fig. 4b), also depict similar water facies like the Piper's diagram, but they further suggest varying degree of mineralization of the water sources. In the OCB, the larger sizes of the stiff diagram for the Lobe soda springs indicate more mineralization than for water from the wells. Likewise in the samples from the continental sector (CS) the water in the Sabga soda springs are most mineralized, followed by those in Bambui and the least mineralized is that from the Nyos soda spring. The observed variation in degree of mineralisation could in part be indicating variation in residence time, where the older springs are enriched in elements from aquifer minerals than in younger springs (e.g., Fantong et al., 2010a; Kamctueng et al., 2015) that are renewed through a local and short recharge-discharge flow paths.

Recharge mechanisms and evaporation of the sampled waters

Isotopic ratios of hydrogen and oxygen, which are used in this study to infer recharge and evaporation mechanisms in the waters are also shown in Table 2 and graphically presented in Fig. 5. The δD values ranged from -41.8 in Sabga A soda spring to -26 ‰ in water from well 5.

Oxygen isotope ($\delta^{18}O$) values range from -6.3 ‰ in Sabga A spring to -3.1 ‰ in water from well 3. Due to the paucity of isotope data on local rainfall, the Global Meteoric Water Line (GMWL) of Craig (1961), which is defined by the line $\delta D = 8\delta^{18}O + 10$ is also presented as a reference. Distribution of sample water in the δD-$\delta^{18}O$ graph suggests that water in the Bambui and Sabga soda springs are subject to little or no evaporation, while the Lobe soda springs suggest slight evaporation, but water from the wells and Nyos soda springs show remarkable evaporation tendencies. Such a pattern depicts that the Bambui and Sabga soda springs are subject to the mechanism of preferential flow pass, which is caused by rapid recharge (e.g., Tsujimura et al., 2007; Asai et al., 2009), that is favored by the highly altered and jointed lavas as opposed to the Lobe and Nyos cave soda springs, and the wells. Except for the Lobe soda springs, the other springs are sources of drinking water for animals (cattle and goats), and a source of minerals (carbonate) for local manufacture of soup for consumption by the nearby population, thus it is important to assess at a preliminary scale the medical hydrogeochemical characteristics of the springs.

Health implications of the water chemistry

Given that the gas bubbling springs are located in the area of livestock rearing and human activities, their chemistry is here preliminarily evaluated to assess potential health implications. With respect to fluoride, Figure 6a shows that except for the Nyos cave soda spring, all the other soda springs contain fluoride at concentrations that are above the WHO optimal limit (1.5 mg/l e.g., Kut et al., 2016). This indicates that the animals and the population that exploit these springs are potentially exposed to fluoride poisoning as reported by Fantong et al. (2010b) in the Far Northern Region of Cameroon. The potential geogenic and volcanic provenance (Davies, 2013), and actual epidemic effects of such high concentrations of fluoride are not within the scope of this study, and need further investigation.

With respect to arsenic (As), Figure 6b shows that the Sabga soda springs contain As at concentrations as high as 1.33 ppm that are above the WHO upper limit (0.03 ppm in drinking water). Based on the field observations that water from the Sabga soda springs is heavily consumed by cattle, and carbonate there-from is exploited for consumption by the population, it is also a challenge for medical geochemists to carry out a comprehensive investigation into the incidence, origin, mobilization and epidiomological effects of arsenic in these areas.

Impact of volcanic volatile or magmatic input on chemistry of the spring water

The dissolved state of elements and saturation state of compounds observed in the springs are to an extent determined by their saturation indices and stoichiometry (e.g., Faure, 1991).

Saturation indices and activity diagrams

The saturation index (SI) of a given mineral in an aqueous system is defined as (Lloyd and Heathcoat, 1985; and Deutch, 1997):

$$\mathrm{SI} = \log\left(\frac{\mathrm{IAP}}{\mathrm{K_{sp}}}\right) \qquad (1)$$

where IAP is the ion activity product and K_{sp} is the solubility product of the mineral in the system. A SI > 0 points to supersaturation, and a tendency for the mineral to precipitate from the water. Saturation can be produced by factors like incongruent dissolution, common ion effect, evaporation, and rapid increase in temperature and CO_2 exsolution (Appelo and Postma, 2005). A SI < 0 points toward undersaturation, and implies that water dissolves the minerals from surrounding rocks. Negative SI value might also reflect that the character of water is either from a formation with insufficient concentrations of the mineral for precipitation to occur (Garrels and Mackenzie, 1967).

The thermodynamic data used in this computation are those contained in the database of 'Phreeqc for Windows'. A plot of the calculated SI (with respect to quartz, anhydrite, aragonite, calcite and dolomite) versus TDS (Fig.7) groups the water samples into three subgroups: subgroup 1, which consists of water from the shallow wells is undersaturated with respect to all the selected phases and has the lowest TDS values that ranged from 63-83 mg/l. The undersaturation of subgroup 1 suggests that no mineral precipitates in the wells as observed on the field. Subgroup 2, which consists of Nyos cave soda spring, Bambui soda spring B and Sabga soda spring B, show supersaturation with respect to quartz, dolomite. On the field, this subgroup is found to be dominantly precipitating trona (a Na-rich carbonate) and dolomite to a lesser extent. Subgroup 3 that consists of the Lobe and Sabga A soda springs, are supersaturated with respect to dolomite, quartz and calcite, and it is actually precipitating more of dolomite, and trona to a lesser extent.

The stability of secondary minerals (Na and Ca montmorillonites, kaolinite, gibbsite) and amorphous quartz in the springs and wells were evaluated by plotting log (a_{Na}/a_H) vs log (a_{H4SiO4})

(the albite system) (Fig. 8a) and log (a $_{Ca2}$/a$_{2H}$) versus log (a$_{H4SiO4}$) (the anorthite system) (Fig. 8b). These diagrams were drawn with the assumption that aluminum was preserved in the weathering product (Appelo and Postma,1993), because the amount of alumina will remain constant in fresh rocks and its altered equivalent. The constant amount in alumina (Al_2O_3) is because an apparent increase in its weight % is actually always caused by a reduction in the weight of the fresh rock to some smaller amount (Faure, 1991). End member compositions were also assumed using equilibrium relationship for standard temperature (25°C) and pressure (1 atmosphere), which approximately reflect the springs and groundwater conditions. Activities of the species were computed using the analytical concentrations and activity coefficient determined by Phreeqc for Windows version 2.1 under the above conditions (Appelo and Postma, 1993). According to the figures, groundwater from the wells span the stability field of kaolinite, while all the soda springs with exception of the Nyos soda spring are in equilibrium within the Na and Ca -montmorillonite stability fields. This concurs with the incidence of clay minerals in the study area (Fantong et al., 2015). Moreover, the presence of kaolinite and montmorillonite in the study area occur as groundmass in the XRD (X-Ray Defraction) peaks of Figures 9b,10b, 11b, 12b, and 14b. A combination of information from the saturation indices and stability diagrams is supported by the presence of precipitating carbonate phases in the soda springs as shown in Fig. 1.

Typology of carbonate phases

The typology of the carbonate phases that precipitate from the observed soda springs is done by describing the morphology by using SEM images, and identifying the carbonate phase by using XRD diagrams and EPMA elemental mapping.

Carbonate from the Nyos cave soda spring

The SEM image in Fig. 9a shows that the carbonate is an association of cluster of powdery amorphous groundmass upon which sub-euhedral crystals developed. This carbonate is identified with XRD peaks (Fig.9b) as a trona (low- syn trisodium hydrogen dehydrate carbonate). To accentuate the trona phase, an elemental EPMA mapping (Fig.9 c, d, e and f) shows the dominance of sodium, traces of calcium and total absence of magnesium.

Carbonate from Sabga A soda spring

The SEM image of Fig. 10a shows that the carbonate is nail-shaped stalactite crystals protruding from a cluster of powdery amorphous groundmass. This carbonate is identified with XRD peaks (Fig.10b) as a dolomite (calcium-magnesium bicarbonate). Dolomite precipitate in this spring is supported by an elemental EPMA mapping (Fig. 10 c, d, e and f), which shows a dominance and remarkable presence of both calcium and magnesium, with traces of sodium.

Carbonate from Sabga B soda spring

The SEM image of Fig. 11a shows that the carbonate is made up of radiating tabular columns of crystals whose faces are edged by bacteria. This carbonate is identified with XRD peaks (Fig. 11b) as a trona (low-syn trisodium hydrogen dehydrate carbonate). The presence of this trona precipitating in this spring is justified by an elemental EPMA mapping (Fig. 11c, d, e and f), which shows a dominance of sodium and an almost absence of calcium and magnesium.

Carbonate from Bambui B soda spring

The SEM image of Fig. 12a shows that the morphology of the carbonate is an intersecting mosaic of tabular crystals whose faces are edged by bacteria. This carbonate is identified with XRD peaks (Fig. 12b) as a trona similar to that of Sabga B. The presence of this trona precipitating in this spring is supported by an elemental EPMA mapping (Fig. 12 c, d, e and f), which shows a dominance of sodium and low content of calcium and magnesium. The disseminated distribution of fluorine, which almost coincide with the distribution of faint calcite suggest the presence of fluorite (CaF), which could be dissolving to enrich the water phase with fluoride as seen in Fig. 13e.

Carbonate from Lobe D soda spring

The SEM image of Fig. 14a shows that the carbonate is a coliform flower-shape radiating crystals, which is colonized by bacteria. This carbonate is identified with XRD peaks (Fig. 14b) as a dolomite. The occurrence of dolomite as the precipitate in this spring is supported by an elemental EPMA mapping (Fig. 14c, d, e and f), which shows high content of both calcium and magnesium, and low content of sodium.

Summarily, the carbonate phases that are precipitating from the studied soda springs along the CVL are dominantly dolomite and trona. The pristine geochemical attributes and characteristics of the carbonate are at a later phase altered (Demeny, 2016) by diatoms and bacteria as shown in Figure 11a and 12a. The incidence of bacteria in such a hydrogeochemical system leaves biogeochemists with another opportunity to assess the incidence and role of bacteria in the soda spring systems.

Origin of the fluids and carbonates

In a bid to identify the formation (sources and paleo temperature) processes that led to the formation of the observed carbonates, we used ^{13}C isotopes, $^{87}Sr/^{86}Sr$, carbonate-water fractionation temperatures, and Cl^- versus F^- plot as geochemical tracers.

Carbonate-water fractionation temperature

Although oxygen-isotope thermometry based on isotopic fractionation of oxygen between carbonates and water dates back to the Mid-1900s, the carbonate-water oxygen isotopic fractionation equations are still being discussed. The use of isotope thermometry is based on several criteria: (i) the temperature dependence of the isotopic fractionation between the investigated compounds (in our case dolomite/trona and water) and (ii) the isotopic compositions of the compounds are known, (iii) the isotopic equilibrium between the compounds can be proven or at least reasonably assumed, and (iv) no subsequent isotopic alteration occurred after the deposition of carbonates. These considerations are valid for inorganic carbonate formation, as biogenic carbonate is severely affected by the organisms' metabolism, resulting in a species-dependent ‘‘vital effect’’ (Demeny et al., 2010 and references therein)

The temperatures at which the carbonate phases precipitate from the springs were calculated by using the empirical equation for the temperature dependence of calcite-water oxygen isotope fractionation from 10 to 70 °C as shown in equations 2 and 3 that were reported by Demeny et al. (2010).

$$1000.\ln\alpha = 17599/T - 29.64 \text{ [for travertines with a temperature range of 30 to 70}^{o}\text{C]} \quad (2)$$

$$1000.\ln\alpha = 17500/T - 29.89 \text{ [for cave deposits for the range 10 to 25}^{o}\text{C]} \quad (3)$$

The variable T are in ^{o}C.

The values obtained suggest that carbonates precipitate from soda springs along the CVL at temperature that varied from 18.5 - 43°C. The lowest fractionation temperatures (18.5 - 18.6°C) occurred in the Sabga soda springs, while the highest (35 - 43°C), occurred in the Lobe soda springs (Table 3). A plot (Fig. 15), shows that with the exception of the dolomite in the 'Sabga A soda spring', the tronas fractionated at lower temperature (~18.5 - 20 °C) than the dolomites, which fractionated at temperature ranging from 35.2 - 43°C. Based on Figure 15, the oxygen isotopes in carbonates precipitating along the Cameroon Volcanic Line yielded an empirical fractionation– temperature equations of:

$$1000.\ln\alpha = -0.2153T + 35.3 \qquad (4)$$

Stable isotopes of ^{13}C, ^{87}Sr/^{86}Sr, and ^{18}O

The observed carbonates (dolomite and trona) facies in the samples showed broad ranges in ^{87}Sr/^{86}Sr, ^{13}C and δ^{18}O. The ^{87}Sr/^{86}Sr ratio varied from 0.706 - 0.713, the ^{13}C varied from -3.09 to 5.22 VPDB and δ^{18}O from -8.4 to -1.4 VPDB as shown in Table 3. Their δ^{13}C values of observed dolomites are close to the range of values reported for carbonates precipitating from seawater (0 -4 VPDB; Veizer et al., 1999; Shah et al., 2012). Indication of marine origin of the dolomites corroborates with field observation, because the dolomite precipitates from the Lobe soda spring located in the OCB of the study area. However, the carbonates (trona) identified in our study area showed relatively depleted δ^{13}C signatures, which may indicate a possible external source of carbon during trona precipitation (Fig. 16) or a temperature dependent fractionation effect (Shah et al., 2012). The depleted δ^{18}O in dolomite from the 49°C Lobe soda springs, may be due to its higher temperatures (thermogenic type) (Bisse et al., 2018), given that precipitation of dolomite from hot springs leads to relatively depleted δ^{18}O ratios (Land, 1983).

With exception of the Lobe soda springs, where ^{87}Sr/^{86}Sr value did not vary between the carbonate and water phases, in the other soda springs (Bambui soda springs A and B, Sabga soda springs A and B, and Nyos cave soda spring), the ^{87}Sr/^{86}Sr ratio shows a decoupling tendency where the water phases contain relatively higher values than the carbonate phases (Fig. 17a). The relatively higher ^{87}Sr/^{86}Sr ratio in the Lobe soda springs may indicate interaction of dolomitizing fluids with radiogenic lithologies (Shah et al., 2012), which commonly occur along the CVL (e.g., Aka et al., 2000; 2001). Moreover, the ^{87}Sr/^{86}Sr versus ^{18}O cross plot (Fig. 17b), shows that the dolomites are richer in ^{87}Sr/^{86}Sr ratio than the tronas. However, the signatures in the dolomite

of the Sabga soda spring “A” together with those in the tronas are closer to those of the marine signatures (McArthur et al., 2001). Such marine signatures in tronas (Na-rich carbonate) within the continental sector of the Cameroon Volcanic Line, may suggest the presence of paleo-continental sabkha environments, where various sodium carbonates have been recorded in tropical regions (Whitten and Brooks, 1972). This suggestion, however, requires further investigation.

Implications for monitoring and hazard mitigation

Volcanogenic sources of fluorine (e.g., Symonds et al., 1987; Symonds et al., 1988; Bellomo et al., 2003) and chlorine (e.g., Keene and Graedel 1995) containing gasses have been reported in active and passive volcanic areas, and recently in the Nyiragongo volcano in Congo (Liotta et al., 2017). As used by the later, we also used a cross plot of chloride versus fluoride (Fig. 18) to infer volcanogenic contribution in the observed springs along the CVL. The figure suggests volcanogenic inputs into the Lobe, Nyos, Sabga A, and Bambui A springs. The implication of a volcanic input to these fluids suggests that they can be used to monitor volcanic activity and thus mitigate hazards, especially in the vicinity of the Lobe spring located close to the currently active Mt. Cameroon. Moreover, the dominant fluids in the Lobe, Nyos, Sabga A, and Bambui A springs are magmatic CO_2 and H_2O (Sano 1990). Water dissolves slightly more in silicic melts than in basaltic melts, whereas CO_2 dissolves more in basaltic than in silicic melts. Kusakabe (2017) reports that the solubility of CO_2 and H_2O in basaltic melts at 1200^{o}C is a function of the total pressure of the volatiles, whose composition in the melt changes as the decompression proceeds. For example, at low pressure the mole fraction of H_2O equals 0.2 and that of CO_2 is 0.8, implying that basaltic melt becomes rich in CO_2 as the magma ascends and the confining pressure reduces, resulting to degassing. If degassing takes place in an open system, CO_2-rich fluid leaves the magma. This solubility-controlled behavior of CO_2 in basaltic magma may explain a CO_2-rich nature of fluids separated from the magma. The ultimate source of CO_2 in the Nyos, Lobe, Sabga A, and Bambui A springs may therefore be derived from the decarbonation of crystallized metasomatic fluids in the subcontinental lithosphere (Aka, 2015; Asaah et al., 2015). The low (-2 to -3 ‰) ^{13}C values of carbonates in the Nyos and Sabga soda spring may also indicate magmatic origin of the CO_2 that contributes in precipitating the carbonates. Thus, the

permanent supply of such CO_2 in the springs provides good sites for monitoring volcanic activity for hazard mitigation.

Conclusions

The chemistry of water in the bubbling soda springs observed along the Cameroon Volcanic Line shows an evaporated Na+K-Cl and non-evaporated Ca+Mg-HCO_3 facies in the ocean continental boundary sector (OCB) and continental sector (CS), respectively. In the OCB, the Lobe soda springs shows more mineralization than water from nearby hand dug wells. This may indicate that spring water (T=49°C) is circulating deeper than the well water. In the continental sector (CS) the water in the Sabga soda springs are the most mineralized, followed by those in Bambui soda spring and the least mineralized is the Nyos soda spring. With exception of the soda springs in the Nyos area, all other studied soda springs contain fluoride from geogenic fluorine at concentrations above the WHO upper limit, whilst concentrations of arsenic (> 0.3 mg/l) that also call for health concern occur in the Sabga soda springs. The observed soda springs are either saturated or super-saturated with respect to quartz, and carbonate phases, which are actually precipitating as dolomite and trona. The carbonate-water fractionation temperature varies from 18.5 - 43°C. X-ray diffraction spectra and chemical mapping by electron probe microanalyzer unraveled that the precipitating carbonates occur as dolomite in the Lobe and Sabga A soda springs, and as trona in the Nyos, Bambui and Sabga B soda springs. Scanning electron microscope (SEM), reveals various morphologies of the carbonates, including amorphous to tabular euhedral tronas, and nail shaped to bacteria-colonized coliform dolomites. Geochemical tracers of ^{13}C, $^{87}Sr/^{86}Sr$, and ^{18}O indicate a dominantly marine provenance of the carbonate. Chloride versus fluoride cross plot suggest a contribution from volcanic volatiles in the Lobe, Nyos, Sabga A, and Bambui A springs. This contribution of a volcanic input to these fluids suggests that they can be used to monitor volcanic activity and thus mitigate hazards, especially in the vicinity of the Lobe spring that is located close to the currently active Mt. Cameroon.

Acknowledgements

We thank the Institute of Geological and Mining Research (IRGM), Yaoundé, for financial and logistical support during sampling. Thanks to the funders (JICA and JST) of SATREPS-IRGM project that provided field and laboratory equipment that were used to generate the data during

this study. We thank all the members of the Department of Environmental Biology and Chemistry, University of Toyama, Japan, for their enriching comments during the preparation of this manuscript. We are also grateful to Prof. Suh Emmanuel and Prof. Loic Peiffer for their review comments that enriched the content of the manuscript.

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Figures captions

Fig. 1. Locations of sampled carbonate depositing soda springs along the Cameroon Volcanic Line (CVL). CS stands for the continental sector of the CVL, and OCB stands for the oceanic continental boundary of the CVL. The locations of Lake Monoun (L. Monoun), Lake Nyos (L. Nyos), and Mount Cameroon (Mt. Cameroon) are also shown. The black dots correspond to samples' locations

Fig.2. Herds of cattle consuming water from the carbonate depositing springs that have been harnessed

Fig. 3. Samples (deposited carbonates and water) collection sites from observed springs

Fig. 4. Water chemistry presented as Piper's diagram (a), and Stiff diagrams (b) for the observed springs

Fig. 5. Plot of δH and $\delta^{18}O$ in water from observed springs. The Sabga and Bambui springs showed no evaporation effect, while the Lobe springs, the Nyos spring and water in shallow wells around Lobe spring were subjected to evaporation relative to the meteoric water lines. Zone 1 represents the soda springs and zone 2 represents shallow groundwater in the Lobe spring neighborhood. LMWL: Local meteoric water line. GMWL: Global meteoric water line

Fig. 6. With respect to fluoride concentrations (a), all the observed soda springs with exception of that in Nyos, contain fluoride above the WHO upper limit of 1.5 mg/l. With respect to Arsenic (As) concntrations (b), the springs in the continental sector contain As above the WHO upper limit

Fig. 7. The plots of saturation indices (SI; with respect to quartz, anhydrite, aragonite, calcite and dolomite) versus total dissolved solid (TDS) for investigated water samples (wells and springs), show three subgroups (1: undersaturated wells. 2: trona precipitating springs. 3: dolomite precipitating springs).

Fig. 8. Stability diagrams for some minerals in the systems Na_2–Al_2O_3–SiO_2–H_2O (a) and CaO–Al_2O_3–SiO_2–H_2O (b) at 25°C

Fig. 9. The scanning electron microscope image (a), X-ray diffraction peaks (b), and electron probe microanalyzer mapping (c,d, e,f) of carbonate precipitate from Nyos cave spring

Fig. 10. The scanning electron microscope image (a), X-ray diffraction peaks (b), and electron probe microanalyzer mapping (c,d, e,f) of carbonate precipitate from the Sabga A spring

Fig. 11. The scanning electron microscope image (a), X-ray diffraction peaks (b), and electron probe microanalyzer mapping (c,d, e,f) of carbonate precipitate from the Sabga B spring

Fig.12. The scanning electron microscope image (a), X-ray diffraction peaks (b), and electron probe microanalyzer mapping (c,d, e,f) of carbonate precipitate from Bambui B spring

Fig. 13. Electron probe microanalyzer mapping of Na, Ca, Mg, and F of carbonate precipitate from Bambui B spring, showing enrichment of fluorine in the matrix of the carbonate

Fig. 14. The scanning electron microscope image (a), X-ray diffraction peaks (b), and electron probe microanalyzer mapping (c,d, e,f) of carbonate precipitate from Lobe D spring

Fig. 15. Carbonates-water oxygen isotopic fractionation temperature in observed soda springs along the CVL. Dolomites fractionated at relatively higher temperatures (35-43°C) than tronas (circum 20°C).

Fig. 16. Plots of ^{13}C and δ^{18}O (PDB), showed observed tronas to be relatively depleted in ^{13} C and enriched in ^{18}O (PDB).

Fig. 17. Except for the Lobe springs that showed highest ^{87}Sr/^{86}Sr ratio, in all the other observed springs the carbonate phases are relatively enriched in ^{87}Sr/^{86}Sr ratio than the water phase (a), and ^{87}Sr/^{86}Sr are relatively depleted in tronas than in dolomites (b)

Fig. 18. Chloride versus fluoride cross plots showing volcanogenic contributions into the Lobe, Bambui and Nyos springs

Table captions

Table 1. Laboratory analytical methods of the carbonates and water phases in observed springs

Table 2. Chemical composition of water from the observed springs and shallow wells. ND: not detected. NM: not measured

Table 3. Fractionation temperature and isotopic compositions of carbonates precipitating from the observed springs

Abstract

A combined study of major ions, δ^{18}O, δD, ^{13}C, ^{87}Sr/^{86}Sr isotopes, X-ray diffraction, scanning electron microscopy, and electron probe microanalyses on springs and spring mineral precipitates along the Cameroon Volcanic Line (CVL) was undertaken to understand water chemistry, and infer the type and origin of the precipitates. The waters are of evaporated Na+K-Cl and non-evaporated Ca+Mg-HCO_3 types, with the more mineralized (electrical conductivity-EC of 13130 µS/cm) Lobe spring inferred to result from interaction of circulating 49°C waters with magmatic volatiles of the active Mt. Cameroon. Water mineralization in the other springs follows the order: Sabga A > Sabga B> Bambui B > Bambui A > Nyos Cave. But for the Nyos Cave spring, all other springs contain fluoride (up to 0.5 - 35.6 mg/l above WHO potable water upper limit). The Sabga spring contains arsenic (up to 1.3 mg/l above the WHO limits). The springs show low fractionation temperatures in the range of 19 – 43 ^{o}C. The Lobe and Sabga A springs are precipitating dolomite ($CaMg(CO_3)_2$), while the Nyos Cave, Bambui A, Bambui B and Sabga B springs precipitate trona (($Na_3H(CO_3)_2.H_2O$). Our data suggest a marine provenance for the carbonates, and point to a volcanic input for the Lobe, Nyos, Sabga A, and Bambui A springs. The latter springs are therefore proposed as proxies for monitoring volcanic activity for hazard mitigation along the CVL.

Key words: *Bubbling springs. Precipitates. Composition. Provenance. Volcanic activity. Hazards mitigation.*

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Major ions, $\delta^{18}O$, $\delta^{13}C$ and $^{87}Sr/^{86}Sr$ compositions of water and precipitates from springs along the Cameroon Volcanic Line (Cameroon, West Africa): Implications for provenance and volcanic hazards

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Abstract

A combined study of major ions, $\delta^{18}O$, δD, ^{13}C, $^{87}Sr/^{86}Sr$ isotopes, X-ray diffraction, scanning electron microscopy, and electron probe microanalyses on springs and spring mineral precipitates along the Cameroon Volcanic Line (CVL) was undertaken to understand water chemistry, and infer the type and origin of the precipitates. The waters are of evaporated Na+K-Cl and non-evaporated Ca+Mg-HCO_3 types, with the more mineralized (electrical conductivity-EC of 13130 µS/cm) Lobe spring inferred to result from interaction of circulating 49°C waters with magmatic volatiles of the active Mt. Cameroon. Water mineralization in the other springs follows the order: Sabga A > Sabga B> Bambui B > Bambui A > Nyos Cave. But for the Nyos Cave spring, all other springs contain fluoride (up to 0.5 - 35.6 mg/l above WHO potable water upper limit). The Sabga spring contains arsenic (up to 1.3 mg/l above the WHO limits). The springs show low fractionation temperatures in the range of 19 – 43 °C. The Lobe and Sabga A springs are precipitating dolomite ($CaMg(CO_3)_2$), while the Nyos Cave, Bambui A, Bambui B

and Sabga B springs precipitate trona ($(Na_3H(CO_3)_2.H_2O)$). Our data suggest a marine provenance for the carbonates, and point to a volcanic input for the Lobe, Nyos, Sabga A, and Bambui A springs. The latter springs are therefore proposed as proxies for monitoring volcanic activity for hazard mitigation along the CVL.

Key words: *Bubbling springs. Precipitates. Composition. Provenance. Volcanic activity. Hazards mitigation.*

Introduction

Mineral-depositing springs are natural systems that offer a good opportunity to study various mechanisms by which waters establish equilibrium with conditions at the Earth's surface (Amundson and Kelly, 1987; Omelon et al., 2006). For example, carbonate-precipitating waters provide an opportunity to evaluate a dynamic carbonate system and the major controls associated with calcite precipitation (Barnes, 1965; Jacobson and Usdowski, 1975), including; isotope fractionation associated with natural calcite precipitation from spring waters (McCrea, 1950; Friedman, 1970; Usdowski et al., 1979; Dandurand et al., 1982; Amundson and Kelly,1987; Usdowski and Hoefs, 1990; Hamilton et al.,1991; Liu et al., 2003), as well as the types, morphologies, textures, and processes involved in the formation of various carbonate phases (Tucker and Bathurst, 1990; Bradley and Eugster, 1969; Ford and Pedley, 1996; Forti, 2005).

Many orifices of gas-water-carbonate interacting systems occur along the Cameroon Volcanic Line (CVL-Fig. 1). Based on carbonate enrichment studies on volcanic debris and springs in part of the continental sector of the CVL (Le Marechal, 1976; Verla et al., 2014); chemical and isotopic characteristics of fluids along the CVL (Tanyileke , 1994); the geochemistry of gases in springs around Mt. Cameroon and Lake Nyos (Kusakabe et al., 1989; Sano et al.,1990; Aka, 1991); the sedimentology and geochemistry of the Bongongo and Ngol travertines along the CVL (Bisse et al., 2018), the following hypotheses have been proposed: (1) the bubbling mineral springs along the CVL contain abundant CO_2. (2) The CO_2 in the bubbling springs is dominantly of magmatic origin. (3) Helium and carbon isotope ratios of gases from a few of the springs

along the CVL revealed a signature similar to hotspot type magma. (4) The precipitating minerals are travertines.

Although these studies provide initial data to understand the geochemical dynamics within the CVL gas-water-carbonate systems, gaps required to better understand the system include; a) a total absence of comprehensive information on the classification and genetic processes of the precipitating carbonates, which is exploited by the indigenes for preparation of traditional soup, b) high concentration (> 100 mg/l) of geogenic fluoride has been reported (e.g., Kut et al., 2016; and references there-in) in thermal waters along the Ethopian rift. Such concentrations of fluoride in water that is used for domestic purposes and livestock rearing can cause tremendous health effects (e.g., Fantong et al., 2010). Livestock rearing on the slopes of the CVL heavily consumes water from the springs (Fig. 2), so there is still a need to re-assess their chemical characteristics with focus on potential harmful elements like fluoride and arsenic, and c) the carbonate-water fractionation temperature remains unknown.

Against this backdrop, the objectives of this study are to 1) characterize the water chemistry with focus on health implications, 2) estimate the carbonate-water fractionation temperature, and 3) identify, describe and classify the carbonates that are precipitating from the springs.

Study area

Figure 1 shows, the sample sites along the CVL, a prominent 1600 km long Y-shaped chain of Tertiary to Recent, generally alkaline volcanoes that overlap an array of dextral faults called the Central Africa Shear Zone (CASZ) (Ngako et al., 2006) on the African continent, comparable only to the East Africa Rift System. The CVL follows a trend of crustal weakness that stretches from the Atlantic Island of Annobon, through the Gulf of Guinea, to the interior of the African continent (Fitton, 1980; Déruelle et al., 1987, Halliday et al., 1988;). It is unique amongst intraplate volcanic provinces in that it straddles the continental margin and includes both oceanic and continental intraplate volcanism. The oceanic sector constitutes a mildly alkaline volcanic series, which evolves towards phonolite, while the continental sector evolves towards rhyolite (e.g., Fitton, 1980). Isotopic studies of lavas (Halliday et al., 1988) divide the CVL into three sectors: an oceanic zone, ocean-continent boundary zone and a continental zone.

The study area overlaps two (coastal and tropical western highlands) of the five climatic zones in Cameroon, with mean annual rainfall of 5000 and 3000 mm, mean annual atmospheric

temperatures of 26°C and 21°C, humidity of 85% and 80%, and evaporation of 600 mm and 700 mm, respectively (Sighomnou, 2004). Hydrologically, three (coastal, Sanaga, and Niger) of the five river basins in Cameroon drain the study area in a dendritic manner. According to Le Marechal (1968) and Tanyileke (1994), riverine and in aquifer waters encounter heat and mantle-derived CO_2 gas that emanate through the CASZ, causing heating and bubbling of the spring systems along the CVL. At each spring site the gas phase manifests as either bubbles or 'rotten egg' smell, while the precipitates occur as white films, white grains in volcanic ash, stalactite and stalactmite in caves, and mounds around orifices as shown in Fig. 3. At the sites of Sabga A in Fig. 3, animals consume the water as a source of salt, while humans exploit the precipitates for food recipes.

Method of study

Water and precipitate samples were collected from selected bubbling soda spring sites along the CVL (Fig. 3) in October 2015. Each water sample was collected in 3 acid-washed 250 ml polyethylene bottles after rinsing them thrice with the sample. At each sampling site, an unfiltered, unacidified and tightly corked sample was collected in one bottle for subsequent analyses for stable environmental isotopes of hydrogen (δ^2H) and oxygen ($\delta^{18}O$). The second bottle contained un-acidified but filtered sample for anion analyses, and the third filtered and acidified sample for cations and trace elements analyses. Prior to sample collection, in-situ physicochemical measurements were recorded for pH (TOA-DKK HM-30P meter), electrical conductivity (TOA-DKK CM-31P EC meter), reduction-oxidation potential (TOA-DKK ORP meter), and water temperature. Geographical parameters (latitude, longitude and altitude) of each sample site were recorded in the field using a hand-held Garmin GPS. Alkalinity was measured using a ‘‘Hach’’ field titration kit, after addition of 0.16 N H_2SO_4 to the sample to reach the endpoint titration (pH 4.5). Samples were filtered through 0.2 μm filters prior to major ions and dissolved silica determination. Three kilograms chunks of massive carbonate was chipped off with a hammer at sites with consolidated precipitate, and 300 g scoped from sites with unconsolidated precipitate. Each precipitate was put in a clean plastic container, sealed and labelled.

Water samples and precipitates were transported to the University of Toyama, in Japan for chemical analyses.

The various chemical analyses that were done in various institutes in Japan are tabulated in Table 1.

Results and Discussions

Variation of water chemistry

Chemical compositions and isotopic ratios of water samples and carbonate phases are presented in Tables 2 and 3. Measured in-situ parameters show values in the range of 54 - 13130 µS/cm for EC, 4.3 - 7.5 for pH, and 19.3 - 47.4°C for water temperature.

The chemistry of the observed water resources determined with the use of the Piper's diagram (Piper, 1944) (Fig. 4a), shows that water from the Lobe soda springs and its nearby hand dug wells, located in the ocean-continent-boundary (OCB) and close to the ocean (Fig. 4a), have a dominant Na+K-Cl signature. On the other hand, water from the soda springs in Sabga, Bambui, and Nyos have dominantly Ca+Mg-HCO_3 signature. The observed disparity in water facies may be due to the proximity of the Lobe springs to the ocean, which impacts the sodium chloride characteristics as accorded in Le Marechal (1976). Whilst in the other springs, an interaction between primary and secondary minerals in rocks and water could be the dominant explanation as also explained by other researchers (Kamctueng et al., 2014; Fantong et al., 2015). The Stiff diagrams for the water chemistry (Fig. 4b), also depict similar water facies like the Piper's diagram, but they further suggest varying degree of mineralization of the water sources. In the OCB, the larger sizes of the stiff diagram for the Lobe soda springs indicate more mineralization than for water from the wells. Likewise in the samples from the continental sector (CS) the water in the Sabga soda springs are most mineralized, followed by those in Bambui and the least mineralized is that from the Nyos soda spring. The observed variation in degree of mineralisation could in part be indicating variation in residence time, where the older springs are enriched in elements from aquifer minerals than in younger springs (e.g., Fantong et al., 2010a; Kamctueng et al., 2015) that are renewed through a local and short recharge-discharge flow paths.

Recharge mechanisms and evaporation of the sampled waters

Isotopic ratios of hydrogen and oxygen, which are used in this study to infer recharge and evaporation mechanisms in the waters are also shown in Table 2 and graphically presented in Fig. 5. The δD values ranged from -41.8 in Sabga A soda spring to -26 ‰ in water from well 5.

Oxygen isotope ($\delta^{18}O$) values range from -6.3 ‰ in Sabga A spring to -3.1 ‰ in water from well 3. Due to the paucity of isotope data on local rainfall, the Global Meteoric Water Line (GMWL) of Craig (1961), which is defined by the line $\delta D = 8\delta^{18}O + 10$ is also presented as a reference. Distribution of sample water in the δD-$\delta^{18}O$ graph suggests that water in the Bambui and Sabga soda springs are subject to little or no evaporation, while the Lobe soda springs suggest slight evaporation, but water from the wells and Nyos soda springs show remarkable evaporation tendencies. Such a pattern depicts that the Bambui and Sabga soda springs are subject to the mechanism of preferential flow pass, which is caused by rapid recharge (e.g., Tsujimura et al., 2007; Asai et al., 2009), that is favored by the highly altered and jointed lavas as opposed to the Lobe and Nyos cave soda springs, and the wells. Except for the Lobe soda springs, the other springs are sources of drinking water for animals (cattle and goats), and a source of minerals (carbonate) for local manufacture of soup for consumption by the nearby population, thus it is important to assess at a preliminary scale the medical hydrogeochemical characteristics of the springs.

Health implications of the water chemistry

Given that the gas bubbling springs are located in the area of livestock rearing and human activities, their chemistry is here preliminarily evaluated to assess potential health implications. With respect to fluoride, Figure 6a shows that except for the Nyos cave soda spring, all the other soda springs contain fluoride at concentrations that are above the WHO optimal limit (1.5 mg/l e.g., Kut et al., 2016). This indicates that the animals and the population that exploit these springs are potentially exposed to fluoride poisoning as reported by Fantong et al. (2010b) in the Far Northern Region of Cameroon. The potential geogenic and volcanic provenance (Davies, 2013), and actual epidemic effects of such high concentrations of fluoride are not within the scope of this study, and need further investigation.

With respect to arsenic (As), Figure 6b shows that the Sabga soda springs contain As at concentrations as high as 1.33 ppm that are above the WHO upper limit (0.03 ppm in drinking water). Based on the field observations that water from the Sabga soda springs is heavily consumed by cattle, and carbonate there-from is exploited for consumption by the population, it is also a challenge for medical geochemists to carry out a comprehensive investigation into the incidence, origin, mobilization and epidiomological effects of arsenic in these areas.

Impact of volcanic volatile or magmatic input on chemistry of the spring water

The dissolved state of elements and saturation state of compounds observed in the springs are to an extent determined by their saturation indices and stoichiometry (e.g., Faure, 1991).

Saturation indices and activity diagrams

The saturation index (SI) of a given mineral in an aqueous system is defined as (Lloyd and Heathcoat, 1985; and Deutch, 1997):

$$\mathrm{SI} = \log\left(\frac{\mathrm{IAP}}{\mathrm{K_{sp}}}\right) \qquad (1)$$

where IAP is the ion activity product and K_{sp} is the solubility product of the mineral in the system. A SI > 0 points to supersaturation, and a tendency for the mineral to precipitate from the water. Saturation can be produced by factors like incongruent dissolution, common ion effect, evaporation, and rapid increase in temperature and CO_2 exsolution (Appelo and Postma, 2005). A SI < 0 points toward undersaturation, and implies that water dissolves the minerals from surrounding rocks. Negative SI value might also reflect that the character of water is either from a formation with insufficient concentrations of the mineral for precipitation to occur (Garrels and Mackenzie, 1967).

The thermodynamic data used in this computation are those contained in the database of 'Phreeqc for Windows'. A plot of the calculated SI (with respect to quartz, anhydrite, aragonite, calcite and dolomite) versus TDS (Fig.7) groups the water samples into three subgroups: subgroup 1, which consists of water from the shallow wells is undersaturated with respect to all the selected phases and has the lowest TDS values that ranged from 63-83 mg/l. The undersaturation of subgroup 1 suggests that no mineral precipitates in the wells as observed on the field. Subgroup 2, which consists of Nyos cave soda spring, Bambui soda spring B and Sabga soda spring B, show supersaturation with respect to quartz, dolomite. On the field, this subgroup is found to be dominantly precipitating trona (a Na-rich carbonate) and dolomite to a lesser extent. Subgroup 3 that consists of the Lobe and Sabga A soda springs, are supersaturated with respect to dolomite, quartz and calcite, and it is actually precipitating more of dolomite, and trona to a lesser extent.

The stability of secondary minerals (Na and Ca montmorillonites, kaolinite, gibbsite) and amorphous quartz in the springs and wells were evaluated by plotting log (a_{Na}/a_{H}) vs log (a_{H4SiO4})

(the albite system) (Fig. 8a) and log (a $_{Ca2}$/a$_{2H}$) versus log (a$_{H4SiO4}$) (the anorthite system) (Fig. 8b). These diagrams were drawn with the assumption that aluminum was preserved in the weathering product (Appelo and Postma,1993), because the amount of alumina will remain constant in fresh rocks and its altered equivalent. The constant amount in alumina (Al_2O_3) is because an apparent increase in its weight % is actually always caused by a reduction in the weight of the fresh rock to some smaller amount (Faure, 1991). End member compositions were also assumed using equilibrium relationship for standard temperature (25°C) and pressure (1 atmosphere), which approximately reflect the springs and groundwater conditions. Activities of the species were computed using the analytical concentrations and activity coefficient determined by Phreeqc for Windows version 2.1 under the above conditions (Appelo and Postma, 1993). According to the figures, groundwater from the wells span the stability field of kaolinite, while all the soda springs with exception of the Nyos soda spring are in equilibrium within the Na and Ca -montmorillonite stability fields. This concurs with the incidence of clay minerals in the study area (Fantong et al., 2015). Moreover, the presence of kaolinite and montmorillonite in the study area occur as groundmass in the XRD (X-Ray Defraction) peaks of Figures 9b,10b, 11b, 12b, and 14b. A combination of information from the saturation indices and stability diagrams is supported by the presence of precipitating carbonate phases in the soda springs as shown in Fig. 1.

Typology of carbonate phases

The typology of the carbonate phases that precipitate from the observed soda springs is done by describing the morphology by using SEM images, and identifying the carbonate phase by using XRD diagrams and EPMA elemental mapping.

Carbonate from the Nyos cave soda spring

The SEM image in Fig. 9a shows that the carbonate is an association of cluster of powdery amorphous groundmass upon which sub-euhedral crystals developed. This carbonate is identified with XRD peaks (Fig.9b) as a trona (low- syn trisodium hydrogen dehydrate carbonate). To accentuate the trona phase, an elemental EPMA mapping (Fig.9 c, d, e and f) shows the dominance of sodium, traces of calcium and total absence of magnesium.

Carbonate from Sabga A soda spring

The SEM image of Fig. 10a shows that the carbonate is nail-shaped stalactite crystals protruding from a cluster of powdery amorphous groundmass. This carbonate is identified with XRD peaks (Fig.10b) as a dolomite (calcium-magnesium bicarbonate). Dolomite precipitate in this spring is supported by an elemental EPMA mapping (Fig. 10 c, d, e and f), which shows a dominance and remarkable presence of both calcium and magnesium, with traces of sodium.

Carbonate from Sabga B soda spring

The SEM image of Fig. 11a shows that the carbonate is made up of radiating tabular columns of crystals whose faces are edged by bacteria. This carbonate is identified with XRD peaks (Fig. 11b) as a trona (low-syn trisodium hydrogen dehydrate carbonate). The presence of this trona precipitating in this spring is justified by an elemental EPMA mapping (Fig. 11c, d, e and f), which shows a dominance of sodium and an almost absence of calcium and magnesium.

Carbonate from Bambui B soda spring

The SEM image of Fig. 12a shows that the morphology of the carbonate is an intersecting mosaic of tabular crystals whose faces are edged by bacteria. This carbonate is identified with XRD peaks (Fig. 12b) as a trona similar to that of Sabga B. The presence of this trona precipitating in this spring is supported by an elemental EPMA mapping (Fig. 12 c, d, e and f), which shows a dominance of sodium and low content of calcium and magnesium. The disseminated distribution of fluorine, which almost coincide with the distribution of faint calcite suggest the presence of fluorite (CaF), which could be dissolving to enrich the water phase with fluoride as seen in Fig. 13e.

Carbonate from Lobe D soda spring

The SEM image of Fig. 14a shows that the carbonate is a coliform flower-shape radiating crystals, which is colonized by bacteria. This carbonate is identified with XRD peaks (Fig. 14b) as a dolomite. The occurrence of dolomite as the precipitate in this spring is supported by an elemental EPMA mapping (Fig. 14c, d, e and f), which shows high content of both calcium and magnesium, and low content of sodium.

Summarily, the carbonate phases that are precipitating from the studied soda springs along the CVL are dominantly dolomite and trona. The pristine geochemical attributes and characteristics of the carbonate are at a later phase altered (Demeny, 2016) by diatoms and bacteria as shown in Figure 11a and 12a. The incidence of bacteria in such a hydrogeochemical system leaves biogeochemists with another opportunity to assess the incidence and role of bacteria in the soda spring systems.

Origin of the fluids and carbonates

In a bid to identify the formation (sources and paleo temperature) processes that led to the formation of the observed carbonates, we used ^{13}C isotopes, ^{87}Sr/^{86}Sr, carbonate-water fractionation temperatures, and Cl^- versus F^- plot as geochemical tracers.

Carbonate-water fractionation temperature

Although oxygen-isotope thermometry based on isotopic fractionation of oxygen between carbonates and water dates back to the Mid-1900s, the carbonate-water oxygen isotopic fractionation equations are still being discussed. The use of isotope thermometry is based on several criteria: (i) the temperature dependence of the isotopic fractionation between the investigated compounds (in our case dolomite/trona and water) and (ii) the isotopic compositions of the compounds are known, (iii) the isotopic equilibrium between the compounds can be proven or at least reasonably assumed, and (iv) no subsequent isotopic alteration occurred after the deposition of carbonates. These considerations are valid for inorganic carbonate formation, as biogenic carbonate is severely affected by the organisms’ metabolism, resulting in a species-dependent ‘‘vital effect’’ (Demeny et al., 2010 and references therein)

The temperatures at which the carbonate phases precipitate from the springs were calculated by using the empirical equation for the temperature dependence of calcite-water oxygen isotope fractionation from 10 to 70 °C as shown in equations 2 and 3 that were reported by Demeny et al. (2010).

$$1000.\ln\alpha = 17599/T - 29.64 \text{ [for travertines with a temperature range of 30 to 70}^{o}\text{C]} \quad (2)$$

$$1000.\ln\alpha = 17500/T - 29.89 \text{ [for cave deposits for the range 10 to 25}^{o}\text{C]} \quad (3)$$

The variable T are in ^{o}C.

The values obtained suggest that carbonates precipitate from soda springs along the CVL at temperature that varied from 18.5 - 43°C. The lowest fractionation temperatures (18.5 - 18.6°C) occurred in the Sabga soda springs, while the highest (35 - 43°C), occurred in the Lobe soda springs (Table 3). A plot (Fig. 15), shows that with the exception of the dolomite in the 'Sabga A soda spring', the tronas fractionated at lower temperature (~18.5 - 20 °C) than the dolomites, which fractionated at temperature ranging from 35.2 - 43°C. Based on Figure 15, the oxygen isotopes in carbonates precipitating along the Cameroon Volcanic Line yielded an empirical fractionation– temperature equations of:

$$1000.\ln\alpha = -0.2153T + 35.3 \qquad (4)$$

Stable isotopes of ^{13}C, $^{87}Sr/^{86}Sr$, and ^{18}O

The observed carbonates (dolomite and trona) facies in the samples showed broad ranges in $^{87}Sr/^{86}Sr$, ^{13}C and $\delta^{18}O$. The $^{87}Sr/^{86}Sr$ ratio varied from 0.706 - 0.713, the ^{13}C varied from -3.09 to 5.22 VPDB and $\delta^{18}O$ from -8.4 to -1.4 VPDB as shown in Table 3. Their $\delta^{13}C$ values of observed dolomites are close to the range of values reported for carbonates precipitating from seawater (0 -4 VPDB; Veizer et al., 1999; Shah et al., 2012). Indication of marine origin of the dolomites corroborates with field observation, because the dolomite precipitates from the Lobe soda spring located in the OCB of the study area. However, the carbonates (trona) identified in our study area showed relatively depleted $\delta^{13}C$ signatures, which may indicate a possible external source of carbon during trona precipitation (Fig. 16) or a temperature dependent fractionation effect (Shah et al., 2012). The depleted $\delta^{18}O$ in dolomite from the 49°C Lobe soda springs, may be due to its higher temperatures (thermogenic type) (Bisse et al., 2018), given that precipitation of dolomite from hot springs leads to relatively depleted $\delta^{18}O$ ratios (Land, 1983).

With exception of the Lobe soda springs, where $^{87}Sr/^{86}Sr$ value did not vary between the carbonate and water phases, in the other soda springs (Bambui soda springs A and B, Sabga soda springs A and B, and Nyos cave soda spring), the $^{87}Sr/^{86}Sr$ ratio shows a decoupling tendency where the water phases contain relatively higher values than the carbonate phases (Fig. 17a). The relatively higher $^{87}Sr/^{86}Sr$ ratio in the Lobe soda springs may indicate interaction of dolomitizing fluids with radiogenic lithologies (Shah et al., 2012), which commonly occur along the CVL (e.g., Aka et al., 2000; 2001). Moreover, the $^{87}Sr/^{86}Sr$ versus ^{18}O cross plot (Fig. 17b), shows that the dolomites are richer in $^{87}Sr/^{86}Sr$ ratio than the tronas. However, the signatures in the dolomite

of the Sabga soda spring “A” together with those in the tronas are closer to those of the marine signatures (McArthur et al., 2001). Such marine signatures in tronas (Na-rich carbonate) within the continental sector of the Cameroon Volcanic Line, may suggest the presence of paleo-continental sabkha environments, where various sodium carbonates have been recorded in tropical regions (Whitten and Brooks, 1972). This suggestion, however, requires further investigation.

Implications for monitoring and hazard mitigation

Volcanogenic sources of fluorine (e.g., Symonds et al., 1987; Symonds et al., 1988; Bellomo et al., 2003) and chlorine (e.g., Keene and Graedel 1995) containing gasses have been reported in active and passive volcanic areas, and recently in the Nyiragongo volcano in Congo (Liotta et al., 2017). As used by the later, we also used a cross plot of chloride versus fluoride (Fig. 18) to infer volcanogenic contribution in the observed springs along the CVL. The figure suggests volcanogenic inputs into the Lobe, Nyos, Sabga A, and Bambui A springs. The implication of a volcanic input to these fluids suggests that they can be used to monitor volcanic activity and thus mitigate hazards, especially in the vicinity of the Lobe spring located close to the currently active Mt. Cameroon. Moreover, the dominant fluids in the Lobe, Nyos, Sabga A, and Bambui A springs are magmatic CO_2 and H_2O (Sano 1990). Water dissolves slightly more in silicic melts than in basaltic melts, whereas CO_2 dissolves more in basaltic than in silicic melts. Kusakabe (2017) reports that the solubility of CO_2 and H_2O in basaltic melts at 1200°C is a function of the total pressure of the volatiles, whose composition in the melt changes as the decompression proceeds. For example, at low pressure the mole fraction of H_2O equals 0.2 and that of CO_2 is 0.8, implying that basaltic melt becomes rich in CO_2 as the magma ascends and the confining pressure reduces, resulting to degassing. If degassing takes place in an open system, CO_2-rich fluid leaves the magma. This solubility-controlled behavior of CO_2 in basaltic magma may explain a CO_2-rich nature of fluids separated from the magma. The ultimate source of CO_2 in the Nyos, Lobe, Sabga A, and Bambui A springs may therefore be derived from the decarbonation of crystallized metasomatic fluids in the subcontinental lithosphere (Aka, 2015; Asaah et al., 2015). The low (-2 to -3 ‰) ^{13}C values of carbonates in the Nyos and Sabga soda spring may also indicate magmatic origin of the CO_2 that contributes in precipitating the carbonates. Thus, the

permanent supply of such CO_2 in the springs provides good sites for monitoring volcanic activity for hazard mitigation.

Conclusions

The chemistry of water in the bubbling soda springs observed along the Cameroon Volcanic Line shows an evaporated Na+K-Cl and non-evaporated Ca+Mg-HCO_3 facies in the ocean continental boundary sector (OCB) and continental sector (CS), respectively. In the OCB, the Lobe soda springs shows more mineralization than water from nearby hand dug wells. This may indicate that spring water (T=49°C) is circulating deeper than the well water. In the continental sector (CS) the water in the Sabga soda springs are the most mineralized, followed by those in Bambui soda spring and the least mineralized is the Nyos soda spring. With exception of the soda springs in the Nyos area, all other studied soda springs contain fluoride from geogenic fluorine at concentrations above the WHO upper limit, whilst concentrations of arsenic (> 0.3 mg/l) that also call for health concern occur in the Sabga soda springs. The observed soda springs are either saturated or super-saturated with respect to quartz, and carbonate phases, which are actually precipitating as dolomite and trona. The carbonate-water fractionation temperature varies from 18.5 - 43°C. X-ray diffraction spectra and chemical mapping by electron probe microanalyzer unraveled that the precipitating carbonates occur as dolomite in the Lobe and Sabga A soda springs, and as trona in the Nyos, Bambui and Sabga B soda springs. Scanning electron microscope (SEM), reveals various morphologies of the carbonates, including amorphous to tabular euhedral tronas, and nail shaped to bacteria-colonized coliform dolomites. Geochemical tracers of ^{13}C, $^{87}Sr/^{86}Sr$, and ^{18}O indicate a dominantly marine provenance of the carbonate. Chloride versus fluoride cross plot suggest a contribution from volcanic volatiles in the Lobe, Nyos, Sabga A, and Bambui A springs. This contribution of a volcanic input to these fluids suggests that they can be used to monitor volcanic activity and thus mitigate hazards, especially in the vicinity of the Lobe spring that is located close to the currently active Mt. Cameroon.

Acknowledgements

We thank the Institute of Geological and Mining Research (IRGM), Yaoundé, for financial and logistical support during sampling. Thanks to the funders (JICA and JST) of SATREPS-IRGM project that provided field and laboratory equipment that were used to generate the data during

this study. We thank all the members of the Department of Environmental Biology and Chemistry, University of Toyama, Japan, for their enriching comments during the preparation of this manuscript. We are also grateful to Prof. Suh Emmanuel and Prof. Loic Peiffer for their review comments that enriched the content of the manuscript.

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Figures captions

Fig. 1. Locations of sampled carbonate depositing soda springs along the Cameroon Volcanic Line (CVL). CS stands for the continental sector of the CVL, and OCB stands for the oceanic continental boundary of the CVL. The locations of Lake Monoun (L. Monoun), Lake Nyos (L. Nyos), and Mount Cameroon (Mt. Cameroon) are also shown. The black dots correspond to samples' locations

Fig.2. Herds of cattle consuming water from the carbonate depositing springs that have been harnessed

Fig. 3. Samples (deposited carbonates and water) collection sites from observed springs

Fig. 4. Water chemistry presented as Piper's diagram (a), and Stiff diagrams (b) for the observed springs

Fig. 5. Plot of δH and $\delta^{18}O$ in water from observed springs. The Sabga and Bambui springs showed no evaporation effect, while the Lobe springs, the Nyos spring and water in shallow wells around Lobe spring were subjected to evaporation relative to the meteoric water lines. Zone 1 represents the soda springs and zone 2 represents shallow groundwater in the Lobe spring neighborhood. LMWL: Local meteoric water line. GMWL: Global meteoric water line

Fig. 6. With respect to fluoride concentrations (a), all the observed soda springs with exception of that in Nyos, contain fluoride above the WHO upper limit of 1.5 mg/l. With respect to Arsenic (As) concntrations (b), the springs in the continental sector contain As above the WHO upper limit

Fig. 7. The plots of saturation indices (SI; with respect to quartz, anhydrite, aragonite, calcite and dolomite) versus total dissolved solid (TDS) for investigated water samples (wells and springs), show three subgroups (1: undersaturated wells. 2: trona precipitating springs. 3: dolomite precipitating springs).

Fig. 8. Stability diagrams for some minerals in the systems Na_2–Al_2O_3–SiO_2–H_2O (a) and CaO–Al_2O_3–SiO_2–H_2O (b) at 25°C

Fig. 9. The scanning electron microscope image (a), X-ray diffraction peaks (b), and electron probe microanalyzer mapping (c,d, e,f) of carbonate precipitate from Nyos cave spring

Fig. 10. The scanning electron microscope image (a), X-ray diffraction peaks (b), and electron probe microanalyzer mapping (c,d, e,f) of carbonate precipitate from the Sabga A spring

Fig. 11. The scanning electron microscope image (a), X-ray diffraction peaks (b), and electron probe microanalyzer mapping (c,d, e,f) of carbonate precipitate from the Sabga B spring

Fig.12. The scanning electron microscope image (a), X-ray diffraction peaks (b), and electron probe microanalyzer mapping (c,d, e,f) of carbonate precipitate from Bambui B spring

Fig. 13. Electron probe microanalyzer mapping of Na, Ca, Mg, and F of carbonate precipitate from Bambui B spring, showing enrichment of fluorine in the matrix of the carbonate

Fig. 14. The scanning electron microscope image (a), X-ray diffraction peaks (b), and electron probe microanalyzer mapping (c,d, e,f) of carbonate precipitate from Lobe D spring

Fig. 15. Carbonates-water oxygen isotopic fractionation temperature in observed soda springs along the CVL. Dolomites fractionated at relatively higher temperatures (35-43°C) than tronas (circum 20°C).

Fig. 16. Plots of ^{13}C and δ^{18}O (PDB), showed observed tronas to be relatively depleted in ^{13} C and enriched in ^{18}O (PDB).

Fig. 17. Except for the Lobe springs that showed highest ^{87}Sr/^{86}Sr ratio, in all the other observed springs the carbonate phases are relatively enriched in ^{87}Sr/^{86}Sr ratio than the water phase (a), and ^{87}Sr/^{86}Sr are relatively depleted in tronas than in dolomites (b)

Fig. 18. Chloride versus fluoride cross plots showing volcanogenic contributions into the Lobe, Bambui and Nyos springs

Table captions

Table 1. Laboratory analytical methods of the carbonates and water phases in observed springs

Table 2. Chemical composition of water from the observed springs and shallow wells. ND: not detected. NM: not measured

Table 3. Fractionation temperature and isotopic compositions of carbonates precipitating from the observed springs

Major ions, $\delta^{18}O$, $\delta^{13}C$ and $^{87}Sr/^{86}Sr$ compositions of water and precipitates from springs along the Cameroon Volcanic Line (Cameroon, West Africa): Implications for provenance and volcanic hazards

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Abstract

A combined study of major ions, $\delta^{18}O$, δD, ^{13}C, $^{87}Sr/^{86}Sr$ isotopes, X-ray diffraction, scanning electron microscopy, and electron probe microanalyses on springs and spring mineral precipitates along the Cameroon Volcanic Line (CVL) was undertaken to understand water chemistry, and infer the type and origin of the precipitates. The waters are of evaporated Na+K-Cl and non-evaporated Ca+Mg-HCO_3 types, with the more mineralized (electrical conductivity-EC of 13130 μS/cm) Lobe spring inferred to result from interaction of circulating 49°C waters with magmatic volatiles of the active Mt. Cameroon. Water mineralization in the other springs follows the order: Sabga A > Sabga B> Bambui B > Bambui A > Nyos Cave. But for the Nyos Cave spring, all other springs contain fluoride (up to 0.5 - 35.6 mg/l above WHO potable water upper limit). The Sabga spring contains arsenic (up to 1.3 mg/l above the WHO limits). The springs show low fractionation temperatures in the range of 19 – 43 °C. The Lobe and Sabga A springs are precipitating dolomite ($CaMg(CO_3)_2$), while the Nyos Cave, Bambui A, Bambui B

and Sabga B springs precipitate trona ($(Na_3H(CO_3)_2.H_2O)$). Our data suggest a marine provenance for the carbonates, and point to a volcanic input for the Lobe, Nyos, Sabga A, and Bambui A springs. The latter springs are therefore proposed as proxies for monitoring volcanic activity for hazard mitigation along the CVL.

Key words: *Bubbling springs. Precipitates. Composition. Provenance. Volcanic activity. Hazards mitigation.*

Introduction

Mineral-depositing springs are natural systems that offer a good opportunity to study various mechanisms by which waters establish equilibrium with conditions at the Earth's surface (Amundson and Kelly, 1987; Omelon et al., 2006). For example, carbonate-precipitating waters provide an opportunity to evaluate a dynamic carbonate system and the major controls associated with calcite precipitation (Barnes, 1965; Jacobson and Usdowski, 1975), including; isotope fractionation associated with natural calcite precipitation from spring waters (McCrea, 1950; Friedman, 1970; Usdowski et al., 1979; Dandurand et al., 1982; Amundson and Kelly,1987; Usdowski and Hoefs, 1990; Hamilton et al.,1991; Liu et al., 2003), as well as the types, morphologies, textures, and processes involved in the formation of various carbonate phases (Tucker and Bathurst, 1990; Bradley and Eugster, 1969; Ford and Pedley, 1996; Forti, 2005).

Many orifices of gas-water-carbonate interacting systems occur along the Cameroon Volcanic Line (CVL-Fig. 1). Based on carbonate enrichment studies on volcanic debris and springs in part of the continental sector of the CVL (Le Marechal, 1976; Verla et al., 2014); chemical and isotopic characteristics of fluids along the CVL (Tanyileke , 1994); the geochemistry of gases in springs around Mt. Cameroon and Lake Nyos (Kusakabe et al., 1989; Sano et al.,1990; Aka, 1991); the sedimentology and geochemistry of the Bongongo and Ngol travertines along the CVL (Bisse et al., 2018), the following hypotheses have been proposed: (1) the bubbling mineral springs along the CVL contain abundant CO_2. (2) The CO_2 in the bubbling springs is dominantly of magmatic origin. (3) Helium and carbon isotope ratios of gases from a few of the springs

along the CVL revealed a signature similar to hotspot type magma. (4) The precipitating minerals are travertines.

Although these studies provide initial data to understand the geochemical dynamics within the CVL gas-water-carbonate systems, gaps required to better understand the system include; a) a total absence of comprehensive information on the classification and genetic processes of the precipitating carbonates, which is exploited by the indigenes for preparation of traditional soup, b) high concentration (> 100 mg/l) of geogenic fluoride has been reported (e.g., Kut et al., 2016; and references there-in) in thermal waters along the Ethopian rift. Such concentrations of fluoride in water that is used for domestic purposes and livestock rearing can cause tremendous health effects (e.g., Fantong et al., 2010). Livestock rearing on the slopes of the CVL heavily consumes water from the springs (Fig. 2), so there is still a need to re-assess their chemical characteristics with focus on potential harmful elements like fluoride and arsenic, and c) the carbonate-water fractionation temperature remains unknown.

Against this backdrop, the objectives of this study are to 1) characterize the water chemistry with focus on health implications, 2) estimate the carbonate-water fractionation temperature, and 3) identify, describe and classify the carbonates that are precipitating from the springs.

Study area

Figure 1 shows, the sample sites along the CVL, a prominent 1600 km long Y-shaped chain of Tertiary to Recent, generally alkaline volcanoes that overlap an array of dextral faults called the Central Africa Shear Zone (CASZ) (Ngako et al., 2006) on the African continent, comparable only to the East Africa Rift System. The CVL follows a trend of crustal weakness that stretches from the Atlantic Island of Annobon, through the Gulf of Guinea, to the interior of the African continent (Fitton, 1980; Déruelle et al., 1987, Halliday et al., 1988;). It is unique amongst intraplate volcanic provinces in that it straddles the continental margin and includes both oceanic and continental intraplate volcanism. The oceanic sector constitutes a mildly alkaline volcanic series, which evolves towards phonolite, while the continental sector evolves towards rhyolite (e.g., Fitton, 1980). Isotopic studies of lavas (Halliday et al., 1988) divide the CVL into three sectors: an oceanic zone, ocean-continent boundary zone and a continental zone.

The study area overlaps two (coastal and tropical western highlands) of the five climatic zones in Cameroon, with mean annual rainfall of 5000 and 3000 mm, mean annual atmospheric

temperatures of 26°C and 21°C, humidity of 85% and 80%, and evaporation of 600 mm and 700 mm, respectively (Sighomnou, 2004). Hydrologically, three (coastal, Sanaga, and Niger) of the five river basins in Cameroon drain the study area in a dendritic manner. According to Le Marechal (1968) and Tanyileke (1994), riverine and in aquifer waters encounter heat and mantle-derived CO_2 gas that emanate through the CASZ, causing heating and bubbling of the spring systems along the CVL. At each spring site the gas phase manifests as either bubbles or 'rotten egg' smell, while the precipitates occur as white films, white grains in volcanic ash, stalactite and stalactmite in caves, and mounds around orifices as shown in Fig. 3. At the sites of Sabga A in Fig. 3, animals consume the water as a source of salt, while humans exploit the precipitates for food recipes.

Method of study

Water and precipitate samples were collected from selected bubbling soda spring sites along the CVL (Fig. 3) in October 2015. Each water sample was collected in 3 acid-washed 250 ml polyethylene bottles after rinsing them thrice with the sample. At each sampling site, an unfiltered, unacidified and tightly corked sample was collected in one bottle for subsequent analyses for stable environmental isotopes of hydrogen (δ^2H) and oxygen ($\delta^{18}O$). The second bottle contained un-acidified but filtered sample for anion analyses, and the third filtered and acidified sample for cations and trace elements analyses. Prior to sample collection, in-situ physicochemical measurements were recorded for pH (TOA-DKK HM-30P meter), electrical conductivity (TOA-DKK CM-31P EC meter), reduction-oxidation potential (TOA-DKK ORP meter), and water temperature. Geographical parameters (latitude, longitude and altitude) of each sample site were recorded in the field using a hand-held Garmin GPS. Alkalinity was measured using a ‘‘Hach’’ field titration kit, after addition of 0.16 N H_2SO_4 to the sample to reach the endpoint titration (pH 4.5). Samples were filtered through 0.2 µm filters prior to major ions and dissolved silica determination. Three kilograms chunks of massive carbonate was chipped off with a hammer at sites with consolidated precipitate, and 300 g scoped from sites with unconsolidated precipitate. Each precipitate was put in a clean plastic container, sealed and labelled.

Water samples and precipitates were transported to the University of Toyama, in Japan for chemical analyses.

The various chemical analyses that were done in various institutes in Japan are tabulated in Table 1.

Results and Discussions

Variation of water chemistry

Chemical compositions and isotopic ratios of water samples and carbonate phases are presented in Tables 2 and 3. Measured in-situ parameters show values in the range of 54 - 13130 μS/cm for EC, 4.3 - 7.5 for pH, and 19.3 - 47.4°C for water temperature.

The chemistry of the observed water resources determined with the use of the Piper's diagram (Piper, 1944) (Fig. 4a), shows that water from the Lobe soda springs and its nearby hand dug wells, located in the ocean-continent-boundary (OCB) and close to the ocean (Fig. 4a), have a dominant Na+K-Cl signature. On the other hand, water from the soda springs in Sabga, Bambui, and Nyos have dominantly Ca+Mg-HCO_3 signature. The observed disparity in water facies may be due to the proximity of the Lobe springs to the ocean, which impacts the sodium chloride characteristics as accorded in Le Marechal (1976). Whilst in the other springs, an interaction between primary and secondary minerals in rocks and water could be the dominant explanation as also explained by other researchers (Kamctueng et al., 2014; Fantong et al., 2015). The Stiff diagrams for the water chemistry (Fig. 4b), also depict similar water facies like the Piper's diagram, but they further suggest varying degree of mineralization of the water sources. In the OCB, the larger sizes of the stiff diagram for the Lobe soda springs indicate more mineralization than for water from the wells. Likewise in the samples from the continental sector (CS) the water in the Sabga soda springs are most mineralized, followed by those in Bambui and the least mineralized is that from the Nyos soda spring. The observed variation in degree of mineralisation could in part be indicating variation in residence time, where the older springs are enriched in elements from aquifer minerals than in younger springs (e.g., Fantong et al., 2010a; Kamctueng et al., 2015) that are renewed through a local and short recharge-discharge flow paths.

Recharge mechanisms and evaporation of the sampled waters

Isotopic ratios of hydrogen and oxygen, which are used in this study to infer recharge and evaporation mechanisms in the waters are also shown in Table 2 and graphically presented in Fig. 5. The δD values ranged from -41.8 in Sabga A soda spring to -26 ‰ in water from well 5.

Oxygen isotope ($\delta^{18}O$) values range from -6.3 ‰ in Sabga A spring to -3.1 ‰ in water from well 3. Due to the paucity of isotope data on local rainfall, the Global Meteoric Water Line (GMWL) of Craig (1961), which is defined by the line $\delta D = 8\delta^{18}O + 10$ is also presented as a reference. Distribution of sample water in the δD-$\delta^{18}O$ graph suggests that water in the Bambui and Sabga soda springs are subject to little or no evaporation, while the Lobe soda springs suggest slight evaporation, but water from the wells and Nyos soda springs show remarkable evaporation tendencies. Such a pattern depicts that the Bambui and Sabga soda springs are subject to the mechanism of preferential flow pass, which is caused by rapid recharge (e.g., Tsujimura et al., 2007; Asai et al., 2009), that is favored by the highly altered and jointed lavas as opposed to the Lobe and Nyos cave soda springs, and the wells. Except for the Lobe soda springs, the other springs are sources of drinking water for animals (cattle and goats), and a source of minerals (carbonate) for local manufacture of soup for consumption by the nearby population, thus it is important to assess at a preliminary scale the medical hydrogeochemical characteristics of the springs.

Health implications of the water chemistry

Given that the gas bubbling springs are located in the area of livestock rearing and human activities, their chemistry is here preliminarily evaluated to assess potential health implications. With respect to fluoride, Figure 6a shows that except for the Nyos cave soda spring, all the other soda springs contain fluoride at concentrations that are above the WHO optimal limit (1.5 mg/l e.g., Kut et al., 2016). This indicates that the animals and the population that exploit these springs are potentially exposed to fluoride poisoning as reported by Fantong et al. (2010b) in the Far Northern Region of Cameroon. The potential geogenic and volcanic provenance (Davies, 2013), and actual epidemic effects of such high concentrations of fluoride are not within the scope of this study, and need further investigation.

With respect to arsenic (As), Figure 6b shows that the Sabga soda springs contain As at concentrations as high as 1.33 ppm that are above the WHO upper limit (0.03 ppm in drinking water). Based on the field observations that water from the Sabga soda springs is heavily consumed by cattle, and carbonate there-from is exploited for consumption by the population, it is also a challenge for medical geochemists to carry out a comprehensive investigation into the incidence, origin, mobilization and epidiomological effects of arsenic in these areas.

Impact of volcanic volatile or magmatic input on chemistry of the spring water

The dissolved state of elements and saturation state of compounds observed in the springs are to an extent determined by their saturation indices and stoichiometry (e.g., Faure, 1991).

Saturation indices and activity diagrams

The saturation index (SI) of a given mineral in an aqueous system is defined as (Lloyd and Heathcoat, 1985; and Deutch, 1997):

$$\mathrm{SI} = \log\left(\frac{\mathrm{IAP}}{\mathrm{K_{sp}}}\right) \qquad (1)$$

where IAP is the ion activity product and K_{sp} is the solubility product of the mineral in the system. A SI > 0 points to supersaturation, and a tendency for the mineral to precipitate from the water. Saturation can be produced by factors like incongruent dissolution, common ion effect, evaporation, and rapid increase in temperature and CO_2 exsolution (Appelo and Postma, 2005). A SI < 0 points toward undersaturation, and implies that water dissolves the minerals from surrounding rocks. Negative SI value might also reflect that the character of water is either from a formation with insufficient concentrations of the mineral for precipitation to occur (Garrels and Mackenzie, 1967).

The thermodynamic data used in this computation are those contained in the database of 'Phreeqc for Windows'. A plot of the calculated SI (with respect to quartz, anhydrite, aragonite, calcite and dolomite) versus TDS (Fig.7) groups the water samples into three subgroups: subgroup 1, which consists of water from the shallow wells is undersaturated with respect to all the selected phases and has the lowest TDS values that ranged from 63-83 mg/l. The undersaturation of subgroup 1 suggests that no mineral precipitates in the wells as observed on the field. Subgroup 2, which consists of Nyos cave soda spring, Bambui soda spring B and Sabga soda spring B, show supersaturation with respect to quartz, dolomite. On the field, this subgroup is found to be dominantly precipitating trona (a Na-rich carbonate) and dolomite to a lesser extent. Subgroup 3 that consists of the Lobe and Sabga A soda springs, are supersaturated with respect to dolomite, quartz and calcite, and it is actually precipitating more of dolomite, and trona to a lesser extent.

The stability of secondary minerals (Na and Ca montmorillonites, kaolinite, gibbsite) and amorphous quartz in the springs and wells were evaluated by plotting log (a_{Na}/a_{H}) vs log (a_{H4SiO4})

(the albite system) (Fig. 8a) and log (a $_{Ca2}$/a$_{2H}$) versus log (a$_{H4SiO4}$) (the anorthite system) (Fig. 8b). These diagrams were drawn with the assumption that aluminum was preserved in the weathering product (Appelo and Postma,1993), because the amount of alumina will remain constant in fresh rocks and its altered equivalent. The constant amount in alumina (Al_2O_3) is because an apparent increase in its weight % is actually always caused by a reduction in the weight of the fresh rock to some smaller amount (Faure, 1991). End member compositions were also assumed using equilibrium relationship for standard temperature (25°C) and pressure (1 atmosphere), which approximately reflect the springs and groundwater conditions. Activities of the species were computed using the analytical concentrations and activity coefficient determined by Phreeqc for Windows version 2.1 under the above conditions (Appelo and Postma, 1993). According to the figures, groundwater from the wells span the stability field of kaolinite, while all the soda springs with exception of the Nyos soda spring are in equilibrium within the Na and Ca -montmorillonite stability fields. This concurs with the incidence of clay minerals in the study area (Fantong et al., 2015). Moreover, the presence of kaolinite and montmorillonite in the study area occur as groundmass in the XRD (X-Ray Defraction) peaks of Figures 9b,10b, 11b, 12b, and 14b. A combination of information from the saturation indices and stability diagrams is supported by the presence of precipitating carbonate phases in the soda springs as shown in Fig. 1.

Typology of carbonate phases

The typology of the carbonate phases that precipitate from the observed soda springs is done by describing the morphology by using SEM images, and identifying the carbonate phase by using XRD diagrams and EPMA elemental mapping.

Carbonate from the Nyos cave soda spring

The SEM image in Fig. 9a shows that the carbonate is an association of cluster of powdery amorphous groundmass upon which sub-euhedral crystals developed. This carbonate is identified with XRD peaks (Fig.9b) as a trona (low- syn trisodium hydrogen dehydrate carbonate). To accentuate the trona phase, an elemental EPMA mapping (Fig.9 c, d, e and f) shows the dominance of sodium, traces of calcium and total absence of magnesium.

Carbonate from Sabga A soda spring

The SEM image of Fig. 10a shows that the carbonate is nail-shaped stalactite crystals protruding from a cluster of powdery amorphous groundmass. This carbonate is identified with XRD peaks (Fig.10b) as a dolomite (calcium-magnesium bicarbonate). Dolomite precipitate in this spring is supported by an elemental EPMA mapping (Fig. 10 c, d, e and f), which shows a dominance and remarkable presence of both calcium and magnesium, with traces of sodium.

Carbonate from Sabga B soda spring

The SEM image of Fig. 11a shows that the carbonate is made up of radiating tabular columns of crystals whose faces are edged by bacteria. This carbonate is identified with XRD peaks (Fig. 11b) as a trona (low-syn trisodium hydrogen dehydrate carbonate). The presence of this trona precipitating in this spring is justified by an elemental EPMA mapping (Fig. 11c, d, e and f), which shows a dominance of sodium and an almost absence of calcium and magnesium.

Carbonate from Bambui B soda spring

The SEM image of Fig. 12a shows that the morphology of the carbonate is an intersecting mosaic of tabular crystals whose faces are edged by bacteria. This carbonate is identified with XRD peaks (Fig. 12b) as a trona similar to that of Sabga B. The presence of this trona precipitating in this spring is supported by an elemental EPMA mapping (Fig. 12 c, d, e and f), which shows a dominance of sodium and low content of calcium and magnesium. The disseminated distribution of fluorine, which almost coincide with the distribution of faint calcite suggest the presence of fluorite (CaF), which could be dissolving to enrich the water phase with fluoride as seen in Fig. 13e.

Carbonate from Lobe D soda spring

The SEM image of Fig. 14a shows that the carbonate is a coliform flower-shape radiating crystals, which is colonized by bacteria. This carbonate is identified with XRD peaks (Fig. 14b) as a dolomite. The occurrence of dolomite as the precipitate in this spring is supported by an elemental EPMA mapping (Fig. 14c, d, e and f), which shows high content of both calcium and magnesium, and low content of sodium.

Summarily, the carbonate phases that are precipitating from the studied soda springs along the CVL are dominantly dolomite and trona. The pristine geochemical attributes and characteristics of the carbonate are at a later phase altered (Demeny, 2016) by diatoms and bacteria as shown in Figure 11a and 12a. The incidence of bacteria in such a hydrogeochemical system leaves biogeochemists with another opportunity to assess the incidence and role of bacteria in the soda spring systems.

Origin of the fluids and carbonates

In a bid to identify the formation (sources and paleo temperature) processes that led to the formation of the observed carbonates, we used ^{13}C isotopes, $^{87}Sr/^{86}Sr$, carbonate-water fractionation temperatures, and Cl^- versus F^- plot as geochemical tracers.

Carbonate-water fractionation temperature

Although oxygen-isotope thermometry based on isotopic fractionation of oxygen between carbonates and water dates back to the Mid-1900s, the carbonate-water oxygen isotopic fractionation equations are still being discussed. The use of isotope thermometry is based on several criteria: (i) the temperature dependence of the isotopic fractionation between the investigated compounds (in our case dolomite/trona and water) and (ii) the isotopic compositions of the compounds are known, (iii) the isotopic equilibrium between the compounds can be proven or at least reasonably assumed, and (iv) no subsequent isotopic alteration occurred after the deposition of carbonates. These considerations are valid for inorganic carbonate formation, as biogenic carbonate is severely affected by the organisms' metabolism, resulting in a species-dependent ''vital effect'' (Demeny et al., 2010 and references therein)

The temperatures at which the carbonate phases precipitate from the springs were calculated by using the empirical equation for the temperature dependence of calcite-water oxygen isotope fractionation from 10 to 70 °C as shown in equations 2 and 3 that were reported by Demeny et al. (2010).

$$1000.\ln\alpha = 17599/T - 29.64 \text{ [for travertines with a temperature range of 30 to 70}^{o}\text{C]} \quad (2)$$

$$1000.\ln\alpha = 17500/T - 29.89 \text{ [for cave deposits for the range 10 to 25}^{o}\text{C]} \quad (3)$$

The variable T are in ^{o}C.

The values obtained suggest that carbonates precipitate from soda springs along the CVL at temperature that varied from 18.5 - 43°C. The lowest fractionation temperatures (18.5 - 18.6°C) occurred in the Sabga soda springs, while the highest (35 - 43°C), occurred in the Lobe soda springs (Table 3). A plot (Fig. 15), shows that with the exception of the dolomite in the 'Sabga A soda spring', the tronas fractionated at lower temperature (~18.5 - 20 °C) than the dolomites, which fractionated at temperature ranging from 35.2 - 43°C. Based on Figure 15, the oxygen isotopes in carbonates precipitating along the Cameroon Volcanic Line yielded an empirical fractionation– temperature equations of:

$$1000.\ln\alpha = -0.2153T + 35.3 \qquad (4)$$

Stable isotopes of ^{13}C, ^{87}Sr/^{86}Sr, and ^{18}O

The observed carbonates (dolomite and trona) facies in the samples showed broad ranges in ^{87}Sr/^{86}Sr, ^{13}C and δ^{18}O. The ^{87}Sr/^{86}Sr ratio varied from 0.706 - 0.713, the ^{13}C varied from -3.09 to 5.22 VPDB and δ^{18}O from -8.4 to -1.4 VPDB as shown in Table 3. Their δ^{13}C values of observed dolomites are close to the range of values reported for carbonates precipitating from seawater (0 -4 VPDB; Veizer et al., 1999; Shah et al., 2012). Indication of marine origin of the dolomites corroborates with field observation, because the dolomite precipitates from the Lobe soda spring located in the OCB of the study area. However, the carbonates (trona) identified in our study area showed relatively depleted δ^{13}C signatures, which may indicate a possible external source of carbon during trona precipitation (Fig. 16) or a temperature dependent fractionation effect (Shah et al., 2012). The depleted δ^{18}O in dolomite from the 49°C Lobe soda springs, may be due to its higher temperatures (thermogenic type) (Bisse et al., 2018), given that precipitation of dolomite from hot springs leads to relatively depleted δ^{18}O ratios (Land, 1983).

With exception of the Lobe soda springs, where ^{87}Sr/^{86}Sr value did not vary between the carbonate and water phases, in the other soda springs (Bambui soda springs A and B, Sabga soda springs A and B, and Nyos cave soda spring), the ^{87}Sr/^{86}Sr ratio shows a decoupling tendency where the water phases contain relatively higher values than the carbonate phases (Fig. 17a). The relatively higher ^{87}Sr/^{86}Sr ratio in the Lobe soda springs may indicate interaction of dolomitizing fluids with radiogenic lithologies (Shah et al., 2012), which commonly occur along the CVL (e.g., Aka et al., 2000; 2001). Moreover, the ^{87}Sr/^{86}Sr versus ^{18}O cross plot (Fig. 17b), shows that the dolomites are richer in ^{87}Sr/^{86}Sr ratio than the tronas. However, the signatures in the dolomite

of the Sabga soda spring “A” together with those in the tronas are closer to those of the marine signatures (McArthur et al., 2001). Such marine signatures in tronas (Na-rich carbonate) within the continental sector of the Cameroon Volcanic Line, may suggest the presence of paleo-continental sabkha environments, where various sodium carbonates have been recorded in tropical regions (Whitten and Brooks, 1972). This suggestion, however, requires further investigation.

Implications for monitoring and hazard mitigation

Volcanogenic sources of fluorine (e.g., Symonds et al., 1987; Symonds et al., 1988; Bellomo et al., 2003) and chlorine (e.g., Keene and Graedel 1995) containing gasses have been reported in active and passive volcanic areas, and recently in the Nyiragongo volcano in Congo (Liotta et al., 2017). As used by the later, we also used a cross plot of chloride versus fluoride (Fig. 18) to infer volcanogenic contribution in the observed springs along the CVL. The figure suggests volcanogenic inputs into the Lobe, Nyos, Sabga A, and Bambui A springs. The implication of a volcanic input to these fluids suggests that they can be used to monitor volcanic activity and thus mitigate hazards, especially in the vicinity of the Lobe spring located close to the currently active Mt. Cameroon. Moreover, the dominant fluids in the Lobe, Nyos, Sabga A, and Bambui A springs are magmatic CO_2 and H_2O (Sano 1990). Water dissolves slightly more in silicic melts than in basaltic melts, whereas CO_2 dissolves more in basaltic than in silicic melts. Kusakabe (2017) reports that the solubility of CO_2 and H_2O in basaltic melts at 1200°C is a function of the total pressure of the volatiles, whose composition in the melt changes as the decompression proceeds. For example, at low pressure the mole fraction of H_2O equals 0.2 and that of CO_2 is 0.8, implying that basaltic melt becomes rich in CO_2 as the magma ascends and the confining pressure reduces, resulting to degassing. If degassing takes place in an open system, CO_2-rich fluid leaves the magma. This solubility-controlled behavior of CO_2 in basaltic magma may explain a CO_2-rich nature of fluids separated from the magma. The ultimate source of CO_2 in the Nyos, Lobe, Sabga A, and Bambui A springs may therefore be derived from the decarbonation of crystallized metasomatic fluids in the subcontinental lithosphere (Aka, 2015; Asaah et al., 2015). The low (-2 to -3 ‰) ^{13}C values of carbonates in the Nyos and Sabga soda spring may also indicate magmatic origin of the CO_2 that contributes in precipitating the carbonates. Thus, the

permanent supply of such CO_2 in the springs provides good sites for monitoring volcanic activity for hazard mitigation.

Conclusions

The chemistry of water in the bubbling soda springs observed along the Cameroon Volcanic Line shows an evaporated Na+K-Cl and non-evaporated Ca+Mg-HCO_3 facies in the ocean continental boundary sector (OCB) and continental sector (CS), respectively. In the OCB, the Lobe soda springs shows more mineralization than water from nearby hand dug wells. This may indicate that spring water (T=49°C) is circulating deeper than the well water. In the continental sector (CS) the water in the Sabga soda springs are the most mineralized, followed by those in Bambui soda spring and the least mineralized is the Nyos soda spring. With exception of the soda springs in the Nyos area, all other studied soda springs contain fluoride from geogenic fluorine at concentrations above the WHO upper limit, whilst concentrations of arsenic (> 0.3 mg/l) that also call for health concern occur in the Sabga soda springs. The observed soda springs are either saturated or super-saturated with respect to quartz, and carbonate phases, which are actually precipitating as dolomite and trona. The carbonate-water fractionation temperature varies from 18.5 - 43°C. X-ray diffraction spectra and chemical mapping by electron probe microanalyzer unraveled that the precipitating carbonates occur as dolomite in the Lobe and Sabga A soda springs, and as trona in the Nyos, Bambui and Sabga B soda springs. Scanning electron microscope (SEM), reveals various morphologies of the carbonates, including amorphous to tabular euhedral tronas, and nail shaped to bacteria-colonized coliform dolomites. Geochemical tracers of ^{13}C, $^{87}Sr/^{86}Sr$, and ^{18}O indicate a dominantly marine provenance of the carbonate. Chloride versus fluoride cross plot suggest a contribution from volcanic volatiles in the Lobe, Nyos, Sabga A, and Bambui A springs. This contribution of a volcanic input to these fluids suggests that they can be used to monitor volcanic activity and thus mitigate hazards, especially in the vicinity of the Lobe spring that is located close to the currently active Mt. Cameroon.

Acknowledgements

We thank the Institute of Geological and Mining Research (IRGM), Yaoundé, for financial and logistical support during sampling. Thanks to the funders (JICA and JST) of SATREPS-IRGM project that provided field and laboratory equipment that were used to generate the data during

this study. We thank all the members of the Department of Environmental Biology and Chemistry, University of Toyama, Japan, for their enriching comments during the preparation of this manuscript. We are also grateful to Prof. Suh Emmanuel and Prof. Loic Peiffer for their review comments that enriched the content of the manuscript.

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Figures captions

Fig. 1. Locations of sampled carbonate depositing soda springs along the Cameroon Volcanic Line (CVL). CS stands for the continental sector of the CVL, and OCB stands for the oceanic continental boundary of the CVL. The locations of Lake Monoun (L. Monoun), Lake Nyos (L. Nyos), and Mount Cameroon (Mt. Cameroon) are also shown. The black dots correspond to samples' locations

Fig.2. Herds of cattle consuming water from the carbonate depositing springs that have been harnessed

Fig. 3. Samples (deposited carbonates and water) collection sites from observed springs

Fig. 4. Water chemistry presented as Piper's diagram (a), and Stiff diagrams (b) for the observed springs

Fig. 5. Plot of δH and $\delta^{18}O$ in water from observed springs. The Sabga and Bambui springs showed no evaporation effect, while the Lobe springs, the Nyos spring and water in shallow wells around Lobe spring were subjected to evaporation relative to the meteoric water lines. Zone 1 represents the soda springs and zone 2 represents shallow groundwater in the Lobe spring neighborhood. LMWL: Local meteoric water line. GMWL: Global meteoric water line

Fig. 6. With respect to fluoride concentrations (a), all the observed soda springs with exception of that in Nyos, contain fluoride above the WHO upper limit of 1.5 mg/l. With respect to Arsenic (As) concntrations (b), the springs in the continental sector contain As above the WHO upper limit

Fig. 7. The plots of saturation indices (SI; with respect to quartz, anhydrite, aragonite, calcite and dolomite) versus total dissolved solid (TDS) for investigated water samples (wells and springs), show three subgroups (1: undersaturated wells. 2: trona precipitating springs. 3: dolomite precipitating springs).

Fig. 8. Stability diagrams for some minerals in the systems Na_2–Al_2O_3–SiO_2–H_2O (a) and CaO–Al_2O_3–SiO_2–H_2O (b) at 25°C

Fig. 9. The scanning electron microscope image (a), X-ray diffraction peaks (b), and electron probe microanalyzer mapping (c,d, e,f) of carbonate precipitate from Nyos cave spring

Fig. 10. The scanning electron microscope image (a), X-ray diffraction peaks (b), and electron probe microanalyzer mapping (c,d, e,f) of carbonate precipitate from the Sabga A spring

Fig. 11. The scanning electron microscope image (a), X-ray diffraction peaks (b), and electron probe microanalyzer mapping (c,d, e,f) of carbonate precipitate from the Sabga B spring

Fig.12. The scanning electron microscope image (a), X-ray diffraction peaks (b), and electron probe microanalyzer mapping (c,d, e,f) of carbonate precipitate from Bambui B spring

Fig. 13. Electron probe microanalyzer mapping of Na, Ca, Mg, and F of carbonate precipitate from Bambui B spring, showing enrichment of fluorine in the matrix of the carbonate

Fig. 14. The scanning electron microscope image (a), X-ray diffraction peaks (b), and electron probe microanalyzer mapping (c,d, e,f) of carbonate precipitate from Lobe D spring

Fig. 15. Carbonates-water oxygen isotopic fractionation temperature in observed soda springs along the CVL. Dolomites fractionated at relatively higher temperatures (35-43°C) than tronas (circum 20°C).

Fig. 16. Plots of ^{13}C and δ^{18}O (PDB), showed observed tronas to be relatively depleted in ^{13} C and enriched in ^{18}O (PDB).

Fig. 17. Except for the Lobe springs that showed highest $^{87}Sr/^{86}Sr$ ratio, in all the other observed springs the carbonate phases are relatively enriched in $^{87}Sr/^{86}Sr$ ratio than the water phase (a), and $^{87}Sr/^{86}Sr$ are relatively depleted in tronas than in dolomites (b)

Fig. 18. Chloride versus fluoride cross plots showing volcanogenic contributions into the Lobe, Bambui and Nyos springs

Table captions

Table 1. Laboratory analytical methods of the carbonates and water phases in observed springs

Table 2. Chemical composition of water from the observed springs and shallow wells. ND: not detected. NM: not measured

Table 3. Fractionation temperature and isotopic compositions of carbonates precipitating from the observed springs

Major ions, δ^{18}O, δ^{13}C and ^{87}Sr/^{86}Sr compositions of water and precipitates from springs along the Cameroon Volcanic Line (Cameroon, West Africa): Implications for provenance and volcanic hazards

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Abstract

A combined study of major ions, δ^{18}O, δD, ^{13}C, ^{87}Sr/^{86}Sr isotopes, X-ray diffraction, scanning electron microscopy, and electron probe microanalyses on springs and spring mineral precipitates along the Cameroon Volcanic Line (CVL) was undertaken to understand water chemistry, and infer the type and origin of the precipitates. The waters are of evaporated Na+K-Cl and non-evaporated Ca+Mg-HCO_3 types, with the more mineralized (electrical conductivity-EC of 13130 μS/cm) Lobe spring inferred to result from interaction of circulating 49°C waters with magmatic volatiles of the active Mt. Cameroon. Water mineralization in the other springs follows the order: Sabga A > Sabga B> Bambui B > Bambui A > Nyos Cave. But for the Nyos Cave spring, all other springs contain fluoride (up to 0.5 - 35.6 mg/l above WHO potable water upper limit). The Sabga spring contains arsenic (up to 1.3 mg/l above the WHO limits). The springs show low fractionation temperatures in the range of 19 – 43 ^{o}C. The Lobe and Sabga A springs are precipitating dolomite ($CaMg(CO_3)_2$), while the Nyos Cave, Bambui A, Bambui B

and Sabga B springs precipitate trona ($(Na_3H(CO_3)_2.H_2O)$). Our data suggest a marine provenance for the carbonates, and point to a volcanic input for the Lobe, Nyos, Sabga A, and Bambui A springs. The latter springs are therefore proposed as proxies for monitoring volcanic activity for hazard mitigation along the CVL.

Key words: *Bubbling springs. Precipitates. Composition. Provenance. Volcanic activity. Hazards mitigation.*

Introduction

Mineral-depositing springs are natural systems that offer a good opportunity to study various mechanisms by which waters establish equilibrium with conditions at the Earth's surface (Amundson and Kelly, 1987; Omelon et al., 2006). For example, carbonate-precipitating waters provide an opportunity to evaluate a dynamic carbonate system and the major controls associated with calcite precipitation (Barnes, 1965; Jacobson and Usdowski, 1975), including; isotope fractionation associated with natural calcite precipitation from spring waters (McCrea, 1950; Friedman, 1970; Usdowski et al., 1979; Dandurand et al., 1982; Amundson and Kelly,1987; Usdowski and Hoefs, 1990; Hamilton et al.,1991; Liu et al., 2003), as well as the types, morphologies, textures, and processes involved in the formation of various carbonate phases (Tucker and Bathurst, 1990; Bradley and Eugster, 1969; Ford and Pedley, 1996; Forti, 2005).

Many orifices of gas-water-carbonate interacting systems occur along the Cameroon Volcanic Line (CVL-Fig. 1). Based on carbonate enrichment studies on volcanic debris and springs in part of the continental sector of the CVL (Le Marechal, 1976; Verla et al., 2014); chemical and isotopic characteristics of fluids along the CVL (Tanyileke , 1994); the geochemistry of gases in springs around Mt. Cameroon and Lake Nyos (Kusakabe et al., 1989; Sano et al.,1990; Aka, 1991); the sedimentology and geochemistry of the Bongongo and Ngol travertines along the CVL (Bisse et al., 2018), the following hypotheses have been proposed: (1) the bubbling mineral springs along the CVL contain abundant CO_2. (2) The CO_2 in the bubbling springs is dominantly of magmatic origin. (3) Helium and carbon isotope ratios of gases from a few of the springs

along the CVL revealed a signature similar to hotspot type magma. (4) The precipitating minerals are travertines.

Although these studies provide initial data to understand the geochemical dynamics within the CVL gas-water-carbonate systems, gaps required to better understand the system include; a) a total absence of comprehensive information on the classification and genetic processes of the precipitating carbonates, which is exploited by the indigenes for preparation of traditional soup, b) high concentration (> 100 mg/l) of geogenic fluoride has been reported (e.g., Kut et al., 2016; and references there-in) in thermal waters along the Ethopian rift. Such concentrations of fluoride in water that is used for domestic purposes and livestock rearing can cause tremendous health effects (e.g., Fantong et al., 2010). Livestock rearing on the slopes of the CVL heavily consumes water from the springs (Fig. 2), so there is still a need to re-assess their chemical characteristics with focus on potential harmful elements like fluoride and arsenic, and c) the carbonate-water fractionation temperature remains unknown.

Against this backdrop, the objectives of this study are to 1) characterize the water chemistry with focus on health implications, 2) estimate the carbonate-water fractionation temperature, and 3) identify, describe and classify the carbonates that are precipitating from the springs.

Study area

Figure 1 shows, the sample sites along the CVL, a prominent 1600 km long Y-shaped chain of Tertiary to Recent, generally alkaline volcanoes that overlap an array of dextral faults called the Central Africa Shear Zone (CASZ) (Ngako et al., 2006) on the African continent, comparable only to the East Africa Rift System. The CVL follows a trend of crustal weakness that stretches from the Atlantic Island of Annobon, through the Gulf of Guinea, to the interior of the African continent (Fitton, 1980; Déruelle et al., 1987, Halliday et al., 1988;). It is unique amongst intraplate volcanic provinces in that it straddles the continental margin and includes both oceanic and continental intraplate volcanism. The oceanic sector constitutes a mildly alkaline volcanic series, which evolves towards phonolite, while the continental sector evolves towards rhyolite (e.g., Fitton, 1980). Isotopic studies of lavas (Halliday et al., 1988) divide the CVL into three sectors: an oceanic zone, ocean-continent boundary zone and a continental zone.

The study area overlaps two (coastal and tropical western highlands) of the five climatic zones in Cameroon, with mean annual rainfall of 5000 and 3000 mm, mean annual atmospheric

temperatures of 26°C and 21°C, humidity of 85% and 80%, and evaporation of 600 mm and 700 mm, respectively (Sighomnou, 2004). Hydrologically, three (coastal, Sanaga, and Niger) of the five river basins in Cameroon drain the study area in a dendritic manner. According to Le Marechal (1968) and Tanyileke (1994), riverine and in aquifer waters encounter heat and mantle-derived CO_2 gas that emanate through the CASZ, causing heating and bubbling of the spring systems along the CVL. At each spring site the gas phase manifests as either bubbles or 'rotten egg' smell, while the precipitates occur as white films, white grains in volcanic ash, stalactite and stalactmite in caves, and mounds around orifices as shown in Fig. 3. At the sites of Sabga A in Fig. 3, animals consume the water as a source of salt, while humans exploit the precipitates for food recipes.

Method of study

Water and precipitate samples were collected from selected bubbling soda spring sites along the CVL (Fig. 3) in October 2015. Each water sample was collected in 3 acid-washed 250 ml polyethylene bottles after rinsing them thrice with the sample. At each sampling site, an unfiltered, unacidified and tightly corked sample was collected in one bottle for subsequent analyses for stable environmental isotopes of hydrogen (δ^2H) and oxygen ($\delta^{18}O$). The second bottle contained un-acidified but filtered sample for anion analyses, and the third filtered and acidified sample for cations and trace elements analyses. Prior to sample collection, in-situ physicochemical measurements were recorded for pH (TOA-DKK HM-30P meter), electrical conductivity (TOA-DKK CM-31P EC meter), reduction-oxidation potential (TOA-DKK ORP meter), and water temperature. Geographical parameters (latitude, longitude and altitude) of each sample site were recorded in the field using a hand-held Garmin GPS. Alkalinity was measured using a ''Hach'' field titration kit, after addition of 0.16 N H_2SO_4 to the sample to reach the endpoint titration (pH 4.5). Samples were filtered through 0.2 μm filters prior to major ions and dissolved silica determination. Three kilograms chunks of massive carbonate was chipped off with a hammer at sites with consolidated precipitate, and 300 g scoped from sites with unconsolidated precipitate. Each precipitate was put in a clean plastic container, sealed and labelled.

Water samples and precipitates were transported to the University of Toyama, in Japan for chemical analyses.

The various chemical analyses that were done in various institutes in Japan are tabulated in Table 1.

Results and Discussions

Variation of water chemistry

Chemical compositions and isotopic ratios of water samples and carbonate phases are presented in Tables 2 and 3. Measured in-situ parameters show values in the range of 54 - 13130 μS/cm for EC, 4.3 - 7.5 for pH, and 19.3 - 47.4°C for water temperature.

The chemistry of the observed water resources determined with the use of the Piper's diagram (Piper, 1944) (Fig. 4a), shows that water from the Lobe soda springs and its nearby hand dug wells, located in the ocean-continent-boundary (OCB) and close to the ocean (Fig. 4a), have a dominant Na+K-Cl signature. On the other hand, water from the soda springs in Sabga, Bambui, and Nyos have dominantly Ca+Mg-HCO_3 signature. The observed disparity in water facies may be due to the proximity of the Lobe springs to the ocean, which impacts the sodium chloride characteristics as accorded in Le Marechal (1976). Whilst in the other springs, an interaction between primary and secondary minerals in rocks and water could be the dominant explanation as also explained by other researchers (Kamctueng et al., 2014; Fantong et al., 2015). The Stiff diagrams for the water chemistry (Fig. 4b), also depict similar water facies like the Piper's diagram, but they further suggest varying degree of mineralization of the water sources. In the OCB, the larger sizes of the stiff diagram for the Lobe soda springs indicate more mineralization than for water from the wells. Likewise in the samples from the continental sector (CS) the water in the Sabga soda springs are most mineralized, followed by those in Bambui and the least mineralized is that from the Nyos soda spring. The observed variation in degree of mineralisation could in part be indicating variation in residence time, where the older springs are enriched in elements from aquifer minerals than in younger springs (e.g., Fantong et al., 2010a; Kamctueng et al., 2015) that are renewed through a local and short recharge-discharge flow paths.

Recharge mechanisms and evaporation of the sampled waters

Isotopic ratios of hydrogen and oxygen, which are used in this study to infer recharge and evaporation mechanisms in the waters are also shown in Table 2 and graphically presented in Fig. 5. The δD values ranged from -41.8 in Sabga A soda spring to -26 ‰ in water from well 5.

Oxygen isotope ($\delta^{18}O$) values range from -6.3 ‰ in Sabga A spring to -3.1 ‰ in water from well 3. Due to the paucity of isotope data on local rainfall, the Global Meteoric Water Line (GMWL) of Craig (1961), which is defined by the line $\delta D = 8\delta^{18}O + 10$ is also presented as a reference. Distribution of sample water in the δD-$\delta^{18}O$ graph suggests that water in the Bambui and Sabga soda springs are subject to little or no evaporation, while the Lobe soda springs suggest slight evaporation, but water from the wells and Nyos soda springs show remarkable evaporation tendencies. Such a pattern depicts that the Bambui and Sabga soda springs are subject to the mechanism of preferential flow pass, which is caused by rapid recharge (e.g., Tsujimura et al., 2007; Asai et al., 2009), that is favored by the highly altered and jointed lavas as opposed to the Lobe and Nyos cave soda springs, and the wells. Except for the Lobe soda springs, the other springs are sources of drinking water for animals (cattle and goats), and a source of minerals (carbonate) for local manufacture of soup for consumption by the nearby population, thus it is important to assess at a preliminary scale the medical hydrogeochemical characteristics of the springs.

Health implications of the water chemistry

Given that the gas bubbling springs are located in the area of livestock rearing and human activities, their chemistry is here preliminarily evaluated to assess potential health implications. With respect to fluoride, Figure 6a shows that except for the Nyos cave soda spring, all the other soda springs contain fluoride at concentrations that are above the WHO optimal limit (1.5 mg/l e.g., Kut et al., 2016). This indicates that the animals and the population that exploit these springs are potentially exposed to fluoride poisoning as reported by Fantong et al. (2010b) in the Far Northern Region of Cameroon. The potential geogenic and volcanic provenance (Davies, 2013), and actual epidemic effects of such high concentrations of fluoride are not within the scope of this study, and need further investigation.

With respect to arsenic (As), Figure 6b shows that the Sabga soda springs contain As at concentrations as high as 1.33 ppm that are above the WHO upper limit (0.03 ppm in drinking water). Based on the field observations that water from the Sabga soda springs is heavily consumed by cattle, and carbonate there-from is exploited for consumption by the population, it is also a challenge for medical geochemists to carry out a comprehensive investigation into the incidence, origin, mobilization and epidiomological effects of arsenic in these areas.

Impact of volcanic volatile or magmatic input on chemistry of the spring water

The dissolved state of elements and saturation state of compounds observed in the springs are to an extent determined by their saturation indices and stoichiometry (e.g., Faure, 1991).

Saturation indices and activity diagrams

The saturation index (SI) of a given mineral in an aqueous system is defined as (Lloyd and Heathcoat, 1985; and Deutch, 1997):

$$\mathrm{SI} = \log\left(\frac{\mathrm{IAP}}{\mathrm{K_{sp}}}\right) \qquad (1)$$

where IAP is the ion activity product and K_{sp} is the solubility product of the mineral in the system. A $SI > 0$ points to supersaturation, and a tendency for the mineral to precipitate from the water. Saturation can be produced by factors like incongruent dissolution, common ion effect, evaporation, and rapid increase in temperature and CO_2 exsolution (Appelo and Postma, 2005). A $SI < 0$ points toward undersaturation, and implies that water dissolves the minerals from surrounding rocks. Negative SI value might also reflect that the character of water is either from a formation with insufficient concentrations of the mineral for precipitation to occur (Garrels and Mackenzie, 1967).

The thermodynamic data used in this computation are those contained in the database of 'Phreeqc for Windows'. A plot of the calculated SI (with respect to quartz, anhydrite, aragonite, calcite and dolomite) versus TDS (Fig.7) groups the water samples into three subgroups: subgroup 1, which consists of water from the shallow wells is undersaturated with respect to all the selected phases and has the lowest TDS values that ranged from 63-83 mg/l. The undersaturation of subgroup 1 suggests that no mineral precipitates in the wells as observed on the field. Subgroup 2, which consists of Nyos cave soda spring, Bambui soda spring B and Sabga soda spring B, show supersaturation with respect to quartz, dolomite. On the field, this subgroup is found to be dominantly precipitating trona (a Na-rich carbonate) and dolomite to a lesser extent. Subgroup 3 that consists of the Lobe and Sabga A soda springs, are supersaturated with respect to dolomite, quartz and calcite, and it is actually precipitating more of dolomite, and trona to a lesser extent.

The stability of secondary minerals (Na and Ca montmorillonites, kaolinite, gibbsite) and amorphous quartz in the springs and wells were evaluated by plotting log (a_{Na}/a_{H}) vs log (a_{H4SiO4})

(the albite system) (Fig. 8a) and log (a $_{Ca2}$/a$_{2H}$) versus log (a$_{H4SiO4}$) (the anorthite system) (Fig. 8b). These diagrams were drawn with the assumption that aluminum was preserved in the weathering product (Appelo and Postma,1993), because the amount of alumina will remain constant in fresh rocks and its altered equivalent. The constant amount in alumina (Al_2O_3) is because an apparent increase in its weight % is actually always caused by a reduction in the weight of the fresh rock to some smaller amount (Faure, 1991). End member compositions were also assumed using equilibrium relationship for standard temperature (25°C) and pressure (1 atmosphere), which approximately reflect the springs and groundwater conditions. Activities of the species were computed using the analytical concentrations and activity coefficient determined by Phreeqc for Windows version 2.1 under the above conditions (Appelo and Postma, 1993). According to the figures, groundwater from the wells span the stability field of kaolinite, while all the soda springs with exception of the Nyos soda spring are in equilibrium within the Na and Ca -montmorillonite stability fields. This concurs with the incidence of clay minerals in the study area (Fantong et al., 2015). Moreover, the presence of kaolinite and montmorillonite in the study area occur as groundmass in the XRD (X-Ray Defraction) peaks of Figures 9b,10b, 11b, 12b, and 14b. A combination of information from the saturation indices and stability diagrams is supported by the presence of precipitating carbonate phases in the soda springs as shown in Fig. 1.

Typology of carbonate phases

The typology of the carbonate phases that precipitate from the observed soda springs is done by describing the morphology by using SEM images, and identifying the carbonate phase by using XRD diagrams and EPMA elemental mapping.

Carbonate from the Nyos cave soda spring

The SEM image in Fig. 9a shows that the carbonate is an association of cluster of powdery amorphous groundmass upon which sub-euhedral crystals developed. This carbonate is identified with XRD peaks (Fig.9b) as a trona (low- syn trisodium hydrogen dehydrate carbonate). To accentuate the trona phase, an elemental EPMA mapping (Fig.9 c, d, e and f) shows the dominance of sodium, traces of calcium and total absence of magnesium.

Carbonate from Sabga A soda spring

The SEM image of Fig. 10a shows that the carbonate is nail-shaped stalactite crystals protruding from a cluster of powdery amorphous groundmass. This carbonate is identified with XRD peaks (Fig.10b) as a dolomite (calcium-magnesium bicarbonate). Dolomite precipitate in this spring is supported by an elemental EPMA mapping (Fig. 10 c, d, e and f), which shows a dominance and remarkable presence of both calcium and magnesium, with traces of sodium.

Carbonate from Sabga B soda spring

The SEM image of Fig. 11a shows that the carbonate is made up of radiating tabular columns of crystals whose faces are edged by bacteria. This carbonate is identified with XRD peaks (Fig. 11b) as a trona (low-syn trisodium hydrogen dehydrate carbonate). The presence of this trona precipitating in this spring is justified by an elemental EPMA mapping (Fig. 11c, d, e and f), which shows a dominance of sodium and an almost absence of calcium and magnesium.

Carbonate from Bambui B soda spring

The SEM image of Fig. 12a shows that the morphology of the carbonate is an intersecting mosaic of tabular crystals whose faces are edged by bacteria. This carbonate is identified with XRD peaks (Fig. 12b) as a trona similar to that of Sabga B. The presence of this trona precipitating in this spring is supported by an elemental EPMA mapping (Fig. 12 c, d, e and f), which shows a dominance of sodium and low content of calcium and magnesium. The disseminated distribution of fluorine, which almost coincide with the distribution of faint calcite suggest the presence of fluorite (CaF), which could be dissolving to enrich the water phase with fluoride as seen in Fig. 13e.

Carbonate from Lobe D soda spring

The SEM image of Fig. 14a shows that the carbonate is a coliform flower-shape radiating crystals, which is colonized by bacteria. This carbonate is identified with XRD peaks (Fig. 14b) as a dolomite. The occurrence of dolomite as the precipitate in this spring is supported by an elemental EPMA mapping (Fig. 14c, d, e and f), which shows high content of both calcium and magnesium, and low content of sodium.

Summarily, the carbonate phases that are precipitating from the studied soda springs along the CVL are dominantly dolomite and trona. The pristine geochemical attributes and characteristics of the carbonate are at a later phase altered (Demeny, 2016) by diatoms and bacteria as shown in Figure 11a and 12a. The incidence of bacteria in such a hydrogeochemical system leaves biogeochemists with another opportunity to assess the incidence and role of bacteria in the soda spring systems.

Origin of the fluids and carbonates

In a bid to identify the formation (sources and paleo temperature) processes that led to the formation of the observed carbonates, we used ^{13}C isotopes, ^{87}Sr/^{86}Sr, carbonate-water fractionation temperatures, and Cl^- versus F^- plot as geochemical tracers.

Carbonate-water fractionation temperature

Although oxygen-isotope thermometry based on isotopic fractionation of oxygen between carbonates and water dates back to the Mid-1900s, the carbonate-water oxygen isotopic fractionation equations are still being discussed. The use of isotope thermometry is based on several criteria: (i) the temperature dependence of the isotopic fractionation between the investigated compounds (in our case dolomite/trona and water) and (ii) the isotopic compositions of the compounds are known, (iii) the isotopic equilibrium between the compounds can be proven or at least reasonably assumed, and (iv) no subsequent isotopic alteration occurred after the deposition of carbonates. These considerations are valid for inorganic carbonate formation, as biogenic carbonate is severely affected by the organisms' metabolism, resulting in a species-dependent ‘‘vital effect’’ (Demeny et al., 2010 and references therein)

The temperatures at which the carbonate phases precipitate from the springs were calculated by using the empirical equation for the temperature dependence of calcite-water oxygen isotope fractionation from 10 to 70 °C as shown in equations 2 and 3 that were reported by Demeny et al. (2010).

$1000.\ln\alpha = 17599/T - 29.64$ [for travertines with a temperature range of 30 to 70^{o}C] (2)

$1000.\ln\alpha = 17500/T - 29.89$ [for cave deposits for the range 10 to 25^{o}C] (3)

The variable T are in ^{o}C.

The values obtained suggest that carbonates precipitate from soda springs along the CVL at temperature that varied from 18.5 - 43°C. The lowest fractionation temperatures (18.5 - 18.6°C) occurred in the Sabga soda springs, while the highest (35 - 43°C), occurred in the Lobe soda springs (Table 3). A plot (Fig. 15), shows that with the exception of the dolomite in the 'Sabga A soda spring', the tronas fractionated at lower temperature (~18.5 - 20 °C) than the dolomites, which fractionated at temperature ranging from 35.2 - 43°C. Based on Figure 15, the oxygen isotopes in carbonates precipitating along the Cameroon Volcanic Line yielded an empirical fractionation– temperature equations of:

$$1000.\ln\alpha = -0.2153T + 35.3 \qquad (4)$$

Stable isotopes of ^{13}C, $^{87}Sr/^{86}Sr$, and ^{18}O

The observed carbonates (dolomite and trona) facies in the samples showed broad ranges in $^{87}Sr/^{86}Sr$, ^{13}C and $\delta^{18}O$. The $^{87}Sr/^{86}Sr$ ratio varied from 0.706 - 0.713, the ^{13}C varied from -3.09 to 5.22 VPDB and $\delta^{18}O$ from -8.4 to -1.4 VPDB as shown in Table 3. Their $\delta^{13}C$ values of observed dolomites are close to the range of values reported for carbonates precipitating from seawater (0 -4 VPDB; Veizer et al., 1999; Shah et al., 2012). Indication of marine origin of the dolomites corroborates with field observation, because the dolomite precipitates from the Lobe soda spring located in the OCB of the study area. However, the carbonates (trona) identified in our study area showed relatively depleted $\delta^{13}C$ signatures, which may indicate a possible external source of carbon during trona precipitation (Fig. 16) or a temperature dependent fractionation effect (Shah et al., 2012). The depleted $\delta^{18}O$ in dolomite from the 49°C Lobe soda springs, may be due to its higher temperatures (thermogenic type) (Bisse et al., 2018), given that precipitation of dolomite from hot springs leads to relatively depleted $\delta^{18}O$ ratios (Land, 1983).

With exception of the Lobe soda springs, where $^{87}Sr/^{86}Sr$ value did not vary between the carbonate and water phases, in the other soda springs (Bambui soda springs A and B, Sabga soda springs A and B, and Nyos cave soda spring), the $^{87}Sr/^{86}Sr$ ratio shows a decoupling tendency where the water phases contain relatively higher values than the carbonate phases (Fig. 17a). The relatively higher $^{87}Sr/^{86}Sr$ ratio in the Lobe soda springs may indicate interaction of dolomitizing fluids with radiogenic lithologies (Shah et al., 2012), which commonly occur along the CVL (e.g., Aka et al., 2000; 2001). Moreover, the $^{87}Sr/^{86}Sr$ versus ^{18}O cross plot (Fig. 17b), shows that the dolomites are richer in $^{87}Sr/^{86}Sr$ ratio than the tronas. However, the signatures in the dolomite

of the Sabga soda spring “A” together with those in the tronas are closer to those of the marine signatures (McArthur et al., 2001). Such marine signatures in tronas (Na-rich carbonate) within the continental sector of the Cameroon Volcanic Line, may suggest the presence of paleo-continental sabkha environments, where various sodium carbonates have been recorded in tropical regions (Whitten and Brooks, 1972). This suggestion, however, requires further investigation.

Implications for monitoring and hazard mitigation

Volcanogenic sources of fluorine (e.g., Symonds et al., 1987; Symonds et al., 1988; Bellomo et al., 2003) and chlorine (e.g., Keene and Graedel 1995) containing gasses have been reported in active and passive volcanic areas, and recently in the Nyiragongo volcano in Congo (Liotta et al., 2017). As used by the later, we also used a cross plot of chloride versus fluoride (Fig. 18) to infer volcanogenic contribution in the observed springs along the CVL. The figure suggests volcanogenic inputs into the Lobe, Nyos, Sabga A, and Bambui A springs. The implication of a volcanic input to these fluids suggests that they can be used to monitor volcanic activity and thus mitigate hazards, especially in the vicinity of the Lobe spring located close to the currently active Mt. Cameroon. Moreover, the dominant fluids in the Lobe, Nyos, Sabga A, and Bambui A springs are magmatic CO_2 and H_2O (Sano 1990). Water dissolves slightly more in silicic melts than in basaltic melts, whereas CO_2 dissolves more in basaltic than in silicic melts. Kusakabe (2017) reports that the solubility of CO_2 and H_2O in basaltic melts at 1200°C is a function of the total pressure of the volatiles, whose composition in the melt changes as the decompression proceeds. For example, at low pressure the mole fraction of H_2O equals 0.2 and that of CO_2 is 0.8, implying that basaltic melt becomes rich in CO_2 as the magma ascends and the confining pressure reduces, resulting to degassing. If degassing takes place in an open system, CO_2-rich fluid leaves the magma. This solubility-controlled behavior of CO_2 in basaltic magma may explain a CO_2-rich nature of fluids separated from the magma. The ultimate source of CO_2 in the Nyos, Lobe, Sabga A, and Bambui A springs may therefore be derived from the decarbonation of crystallized metasomatic fluids in the subcontinental lithosphere (Aka, 2015; Asaah et al., 2015). The low (-2 to -3 ‰) ^{13}C values of carbonates in the Nyos and Sabga soda spring may also indicate magmatic origin of the CO_2 that contributes in precipitating the carbonates. Thus, the

permanent supply of such CO_2 in the springs provides good sites for monitoring volcanic activity for hazard mitigation.

Conclusions

The chemistry of water in the bubbling soda springs observed along the Cameroon Volcanic Line shows an evaporated Na+K-Cl and non-evaporated Ca+Mg-HCO_3 facies in the ocean continental boundary sector (OCB) and continental sector (CS), respectively. In the OCB, the Lobe soda springs shows more mineralization than water from nearby hand dug wells. This may indicate that spring water (T=49°C) is circulating deeper than the well water. In the continental sector (CS) the water in the Sabga soda springs are the most mineralized, followed by those in Bambui soda spring and the least mineralized is the Nyos soda spring. With exception of the soda springs in the Nyos area, all other studied soda springs contain fluoride from geogenic fluorine at concentrations above the WHO upper limit, whilst concentrations of arsenic (> 0.3 mg/l) that also call for health concern occur in the Sabga soda springs. The observed soda springs are either saturated or super-saturated with respect to quartz, and carbonate phases, which are actually precipitating as dolomite and trona. The carbonate-water fractionation temperature varies from 18.5 - 43°C. X-ray diffraction spectra and chemical mapping by electron probe microanalyzer unraveled that the precipitating carbonates occur as dolomite in the Lobe and Sabga A soda springs, and as trona in the Nyos, Bambui and Sabga B soda springs. Scanning electron microscope (SEM), reveals various morphologies of the carbonates, including amorphous to tabular euhedral tronas, and nail shaped to bacteria-colonized coliform dolomites. Geochemical tracers of ^{13}C, $^{87}Sr/^{86}Sr$, and ^{18}O indicate a dominantly marine provenance of the carbonate. Chloride versus fluoride cross plot suggest a contribution from volcanic volatiles in the Lobe, Nyos, Sabga A, and Bambui A springs. This contribution of a volcanic input to these fluids suggests that they can be used to monitor volcanic activity and thus mitigate hazards, especially in the vicinity of the Lobe spring that is located close to the currently active Mt. Cameroon.

Acknowledgements

We thank the Institute of Geological and Mining Research (IRGM), Yaoundé, for financial and logistical support during sampling. Thanks to the funders (JICA and JST) of SATREPS-IRGM project that provided field and laboratory equipment that were used to generate the data during

this study. We thank all the members of the Department of Environmental Biology and Chemistry, University of Toyama, Japan, for their enriching comments during the preparation of this manuscript. We are also grateful to Prof. Suh Emmanuel and Prof. Loic Peiffer for their review comments that enriched the content of the manuscript.

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Figures captions

Fig. 1. Locations of sampled carbonate depositing soda springs along the Cameroon Volcanic Line (CVL). CS stands for the continental sector of the CVL, and OCB stands for the oceanic continental boundary of the CVL. The locations of Lake Monoun (L. Monoun), Lake Nyos (L. Nyos), and Mount Cameroon (Mt. Cameroon) are also shown. The black dots correspond to samples' locations

Fig.2. Herds of cattle consuming water from the carbonate depositing springs that have been harnessed

Fig. 3. Samples (deposited carbonates and water) collection sites from observed springs

Fig. 4. Water chemistry presented as Piper's diagram (a), and Stiff diagrams (b) for the observed springs

Fig. 5. Plot of δH and $\delta^{18}O$ in water from observed springs. The Sabga and Bambui springs showed no evaporation effect, while the Lobe springs, the Nyos spring and water in shallow wells around Lobe spring were subjected to evaporation relative to the meteoric water lines. Zone 1 represents the soda springs and zone 2 represents shallow groundwater in the Lobe spring neighborhood. LMWL: Local meteoric water line. GMWL: Global meteoric water line

Fig. 6. With respect to fluoride concentrations (a), all the observed soda springs with exception of that in Nyos, contain fluoride above the WHO upper limit of 1.5 mg/l. With respect to Arsenic (As) concntrations (b), the springs in the continental sector contain As above the WHO upper limit

Fig. 7. The plots of saturation indices (SI; with respect to quartz, anhydrite, aragonite, calcite and dolomite) versus total dissolved solid (TDS) for investigated water samples (wells and springs), show three subgroups (1: undersaturated wells. 2: trona precipitating springs. 3: dolomite precipitating springs).

Fig. 8. Stability diagrams for some minerals in the systems Na_2–Al_2O_3–SiO_2–H_2O (a) and CaO–Al_2O_3–SiO_2–H_2O (b) at 25°C

Fig. 9. The scanning electron microscope image (a), X-ray diffraction peaks (b), and electron probe microanalyzer mapping (c,d, e,f) of carbonate precipitate from Nyos cave spring

Fig. 10. The scanning electron microscope image (a), X-ray diffraction peaks (b), and electron probe microanalyzer mapping (c,d, e,f) of carbonate precipitate from the Sabga A spring

Fig. 11. The scanning electron microscope image (a), X-ray diffraction peaks (b), and electron probe microanalyzer mapping (c,d, e,f) of carbonate precipitate from the Sabga B spring

Fig.12. The scanning electron microscope image (a), X-ray diffraction peaks (b), and electron probe microanalyzer mapping (c,d, e,f) of carbonate precipitate from Bambui B spring

Fig. 13. Electron probe microanalyzer mapping of Na, Ca, Mg, and F of carbonate precipitate from Bambui B spring, showing enrichment of fluorine in the matrix of the carbonate

Fig. 14. The scanning electron microscope image (a), X-ray diffraction peaks (b), and electron probe microanalyzer mapping (c,d, e,f) of carbonate precipitate from Lobe D spring

Fig. 15. Carbonates-water oxygen isotopic fractionation temperature in observed soda springs along the CVL. Dolomites fractionated at relatively higher temperatures (35-43°C) than tronas (circum 20°C).

Fig. 16. Plots of ^{13}C and δ^{18}O (PDB), showed observed tronas to be relatively depleted in ^{13} C and enriched in ^{18}O (PDB).

Fig. 17. Except for the Lobe springs that showed highest ^{87}Sr/^{86}Sr ratio, in all the other observed springs the carbonate phases are relatively enriched in ^{87}Sr/^{86}Sr ratio than the water phase (a), and ^{87}Sr/^{86}Sr are relatively depleted in tronas than in dolomites (b)

Fig. 18. Chloride versus fluoride cross plots showing volcanogenic contributions into the Lobe, Bambui and Nyos springs

Table captions

Table 1. Laboratory analytical methods of the carbonates and water phases in observed springs

Table 2. Chemical composition of water from the observed springs and shallow wells. ND: not detected. NM: not measured

Table 3. Fractionation temperature and isotopic compositions of carbonates precipitating from the observed springs

Table 2

Table 2 :

Sample name	Code	Elevation	Temp	pH	EC	Na$^+$	K$^+$	Mg^{2+}	Ca^{2+}	SiO$_2$	F$^-$	Cl$^-$	NO$_3^-$	SO$_4^{2-}$	HCO$_3^-$	As	δD	δ^{18}O	^{87}Sr/^{86}Sr
		m.asl	ºC	-	µS/cm	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	ppm	‰	‰	water
Bambui Bssp	WS12	1290	22.2	7.0	1650	214	22.2	95.9	248.1	49.12	2	4.8	2.03	4.8	994.4	ND	-36.21	-6.30	0.708618 ± 0.000017
Bambui Assp	WS14	2082	21.8	7.4	1010	351	16.51	21	277.7	17.7	6.78	31.1	1.8	0.36	147.7	ND	-39.41	-6.10	0.70873 ± 0.000021
Lobe Assp	WS10	30	47.4	6.4	12840	1650	70	95	28.2	24.5	35	2130	22.6	113.9	2118	0.009	-32.21	-4.68	0.713340 ± 0.000015
Lobe Dssp	WS9	30	49.0	6.4	13130	1630	66.6	78.64	382.85	25.1	37.1	2198	22.22	99.81	652.9	0.007	-34.76	-4.65	0.713343 ± 0.000013
SabgaA ssp	WS7	1456	20.0	7.5	10710	1240	46.7	13.1	224.4	20.5	3.7	1.59	0.19	6.52	3103	1.33	-41.82	-6.30	0.708808 ± 0.000024
SabgaB ssp	WS6	1535	19.3	7.2	5030	243	79	76.5	275	14.8	4.3	229	0.69	6.72	747	0.015	-39.84	-6.01	0.709314 ± 0.000026
Well 1	WW1	49	27.7	4.5	145	9.94	1.21	0.78	3.06	3.05	0.04	14.7	3.8	23	0.67	ND	-27.94	-3.35	NM
Well 2	WW2	39	28.0	4.9	87	15.69	0.59	1.13	2.79	4.22	0.5	24.95	5.01	5.09	7.32	ND	-30.55	-3.37	NM
Well 3	WW3	51	27.0	4.3	109	7.22	0.78	1.7	3.6	3.38	0.08	10.72	2.57	2.5	13.42	ND	-29.98	-3.1	NM
Well 4	WW4	54	26.0	5.2	54	9.89	1.99	0.5	7.6	5.99	0.19	17.75	8.06	2.33	3.72	ND	-26	-3.27	NM
Well 5	WW5	46	27.0	5.7	229	14.3	1.64	0.75	6.1	9.7	0.19	23.07	9.31	3.98	8.54	ND	NM	NM	NM
Well 6	WW6	51	28.0	6.0	482	322	10.2	46.1	62.4	6.54	1.8	87.33	5.81	261.9	567.4	ND	-31.67	-3.35	0.705157 ± 0.000014
Nyos sodaCssp	NS1	1000	24.0	5.4	198	11.7	422	15	13.2	3.4	0.09	0.6	0.24	1.6	137	ND	-31.12	-3.40	0.70746 ± 0.000029
Nyos soda	NS2	1000	23.0	5.7	536	26	8.11	43	28	4.1	0.01	1.26	0.04	4.15	346	ND	-31.22	-3.59	0.707 ± 0.000014

Figure 1

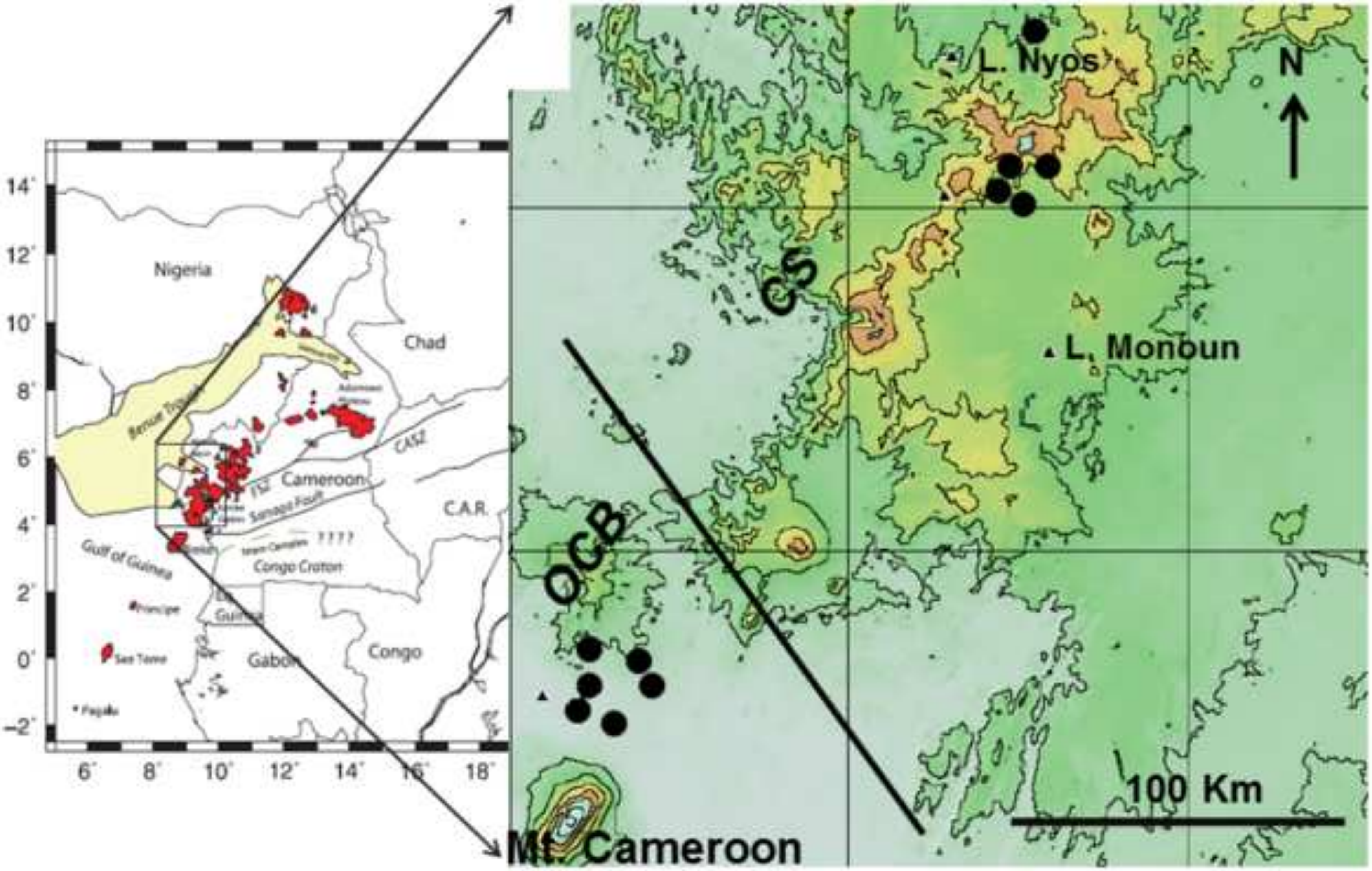
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Figure 2

Figure 3

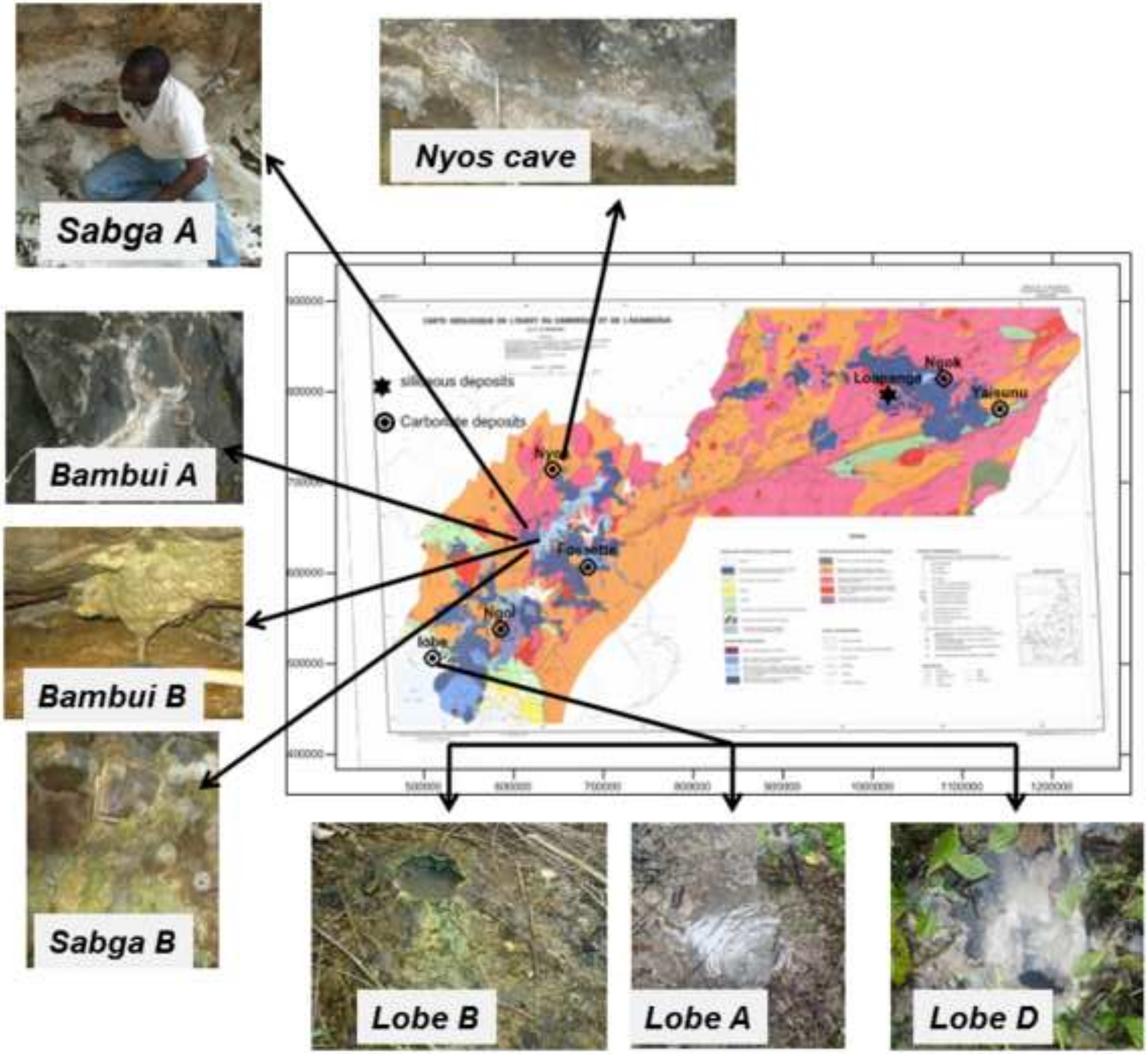
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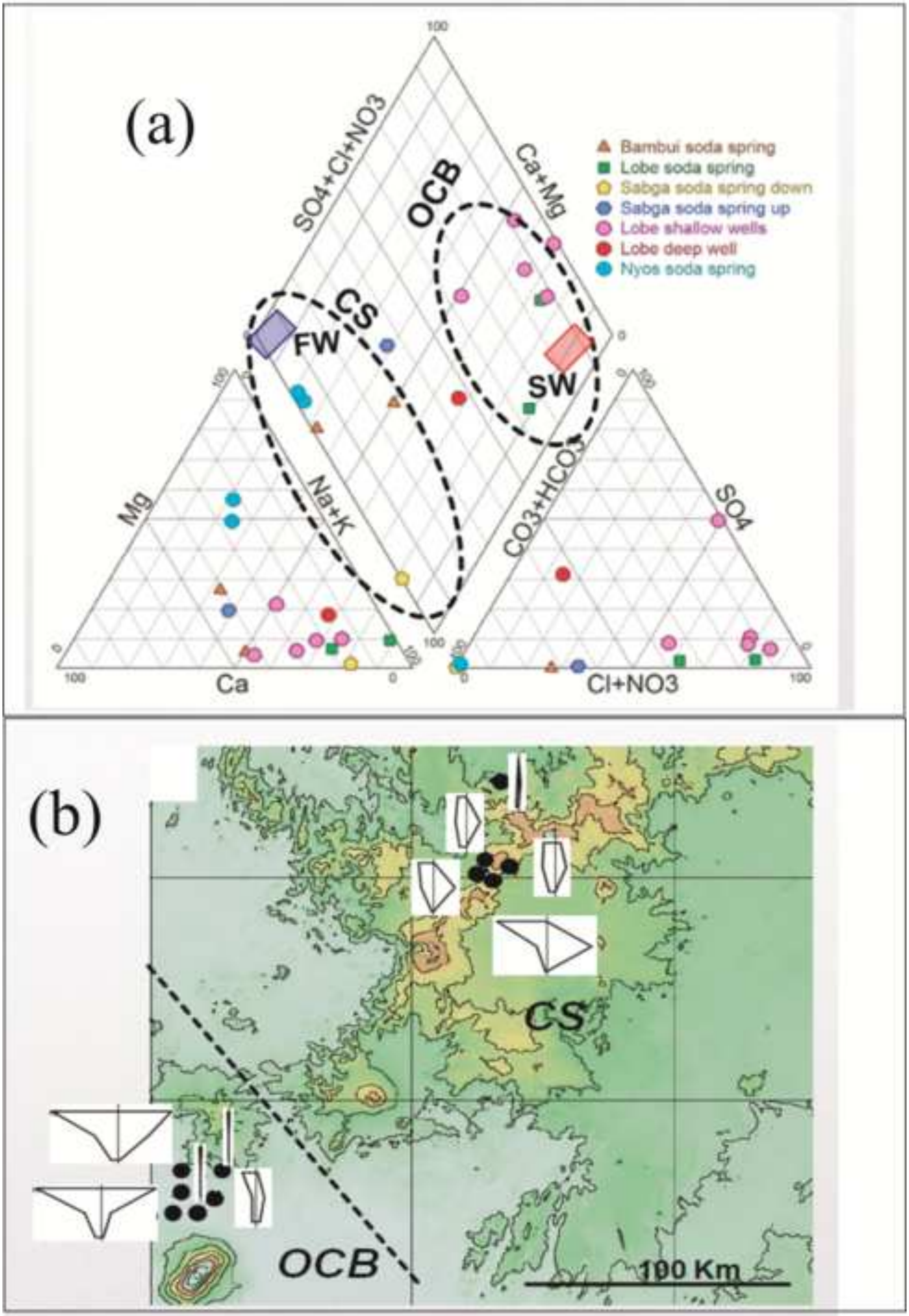
Figure 4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Cl+NO3
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Bambui soda spring
Lobe soda spring
Sabga soda spring down
Sabga soda spring up
Lobe shallow wells
Lobe deep well
Nyos soda spring
(b)
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Figure 5

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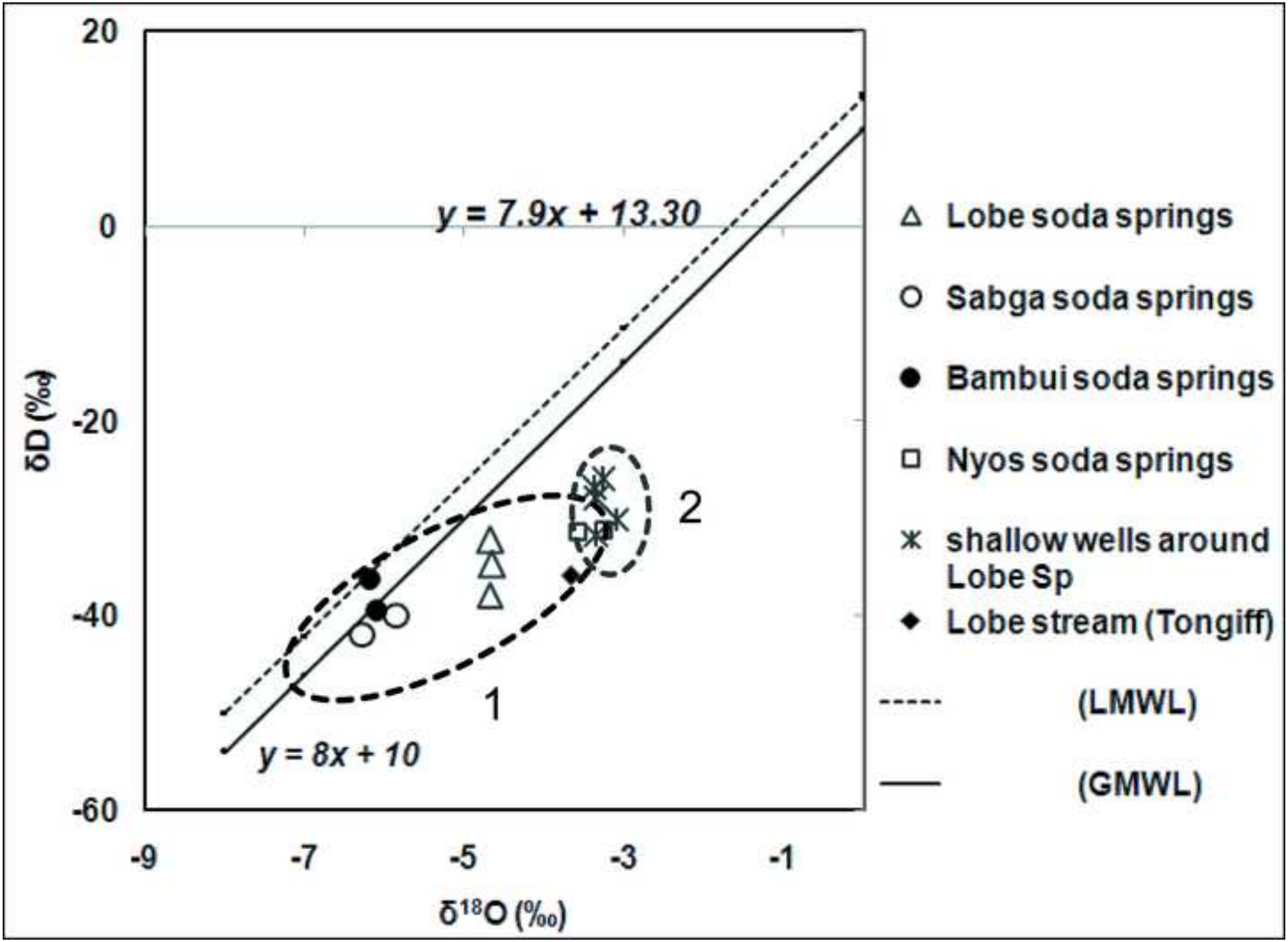

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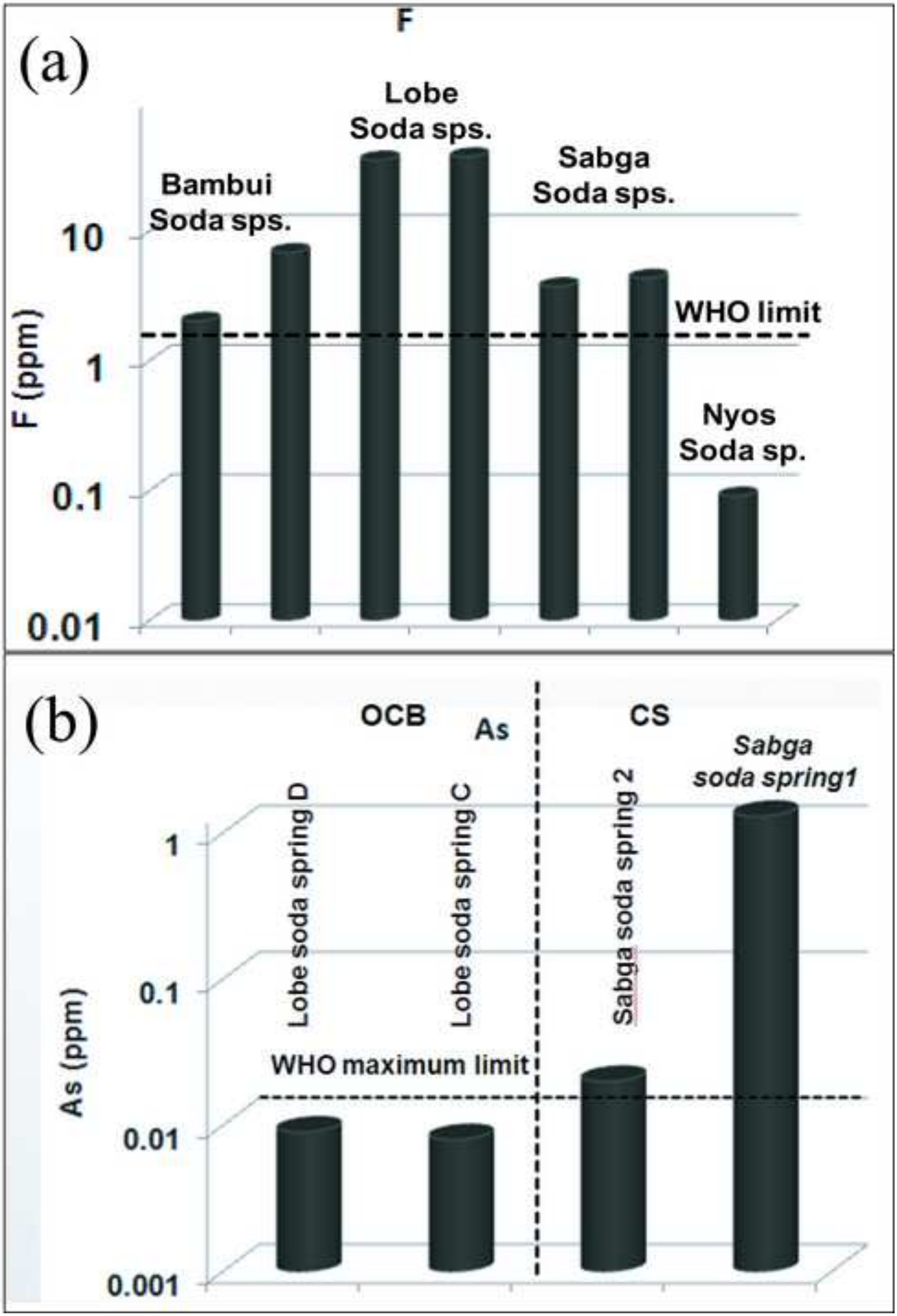
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Figure 7

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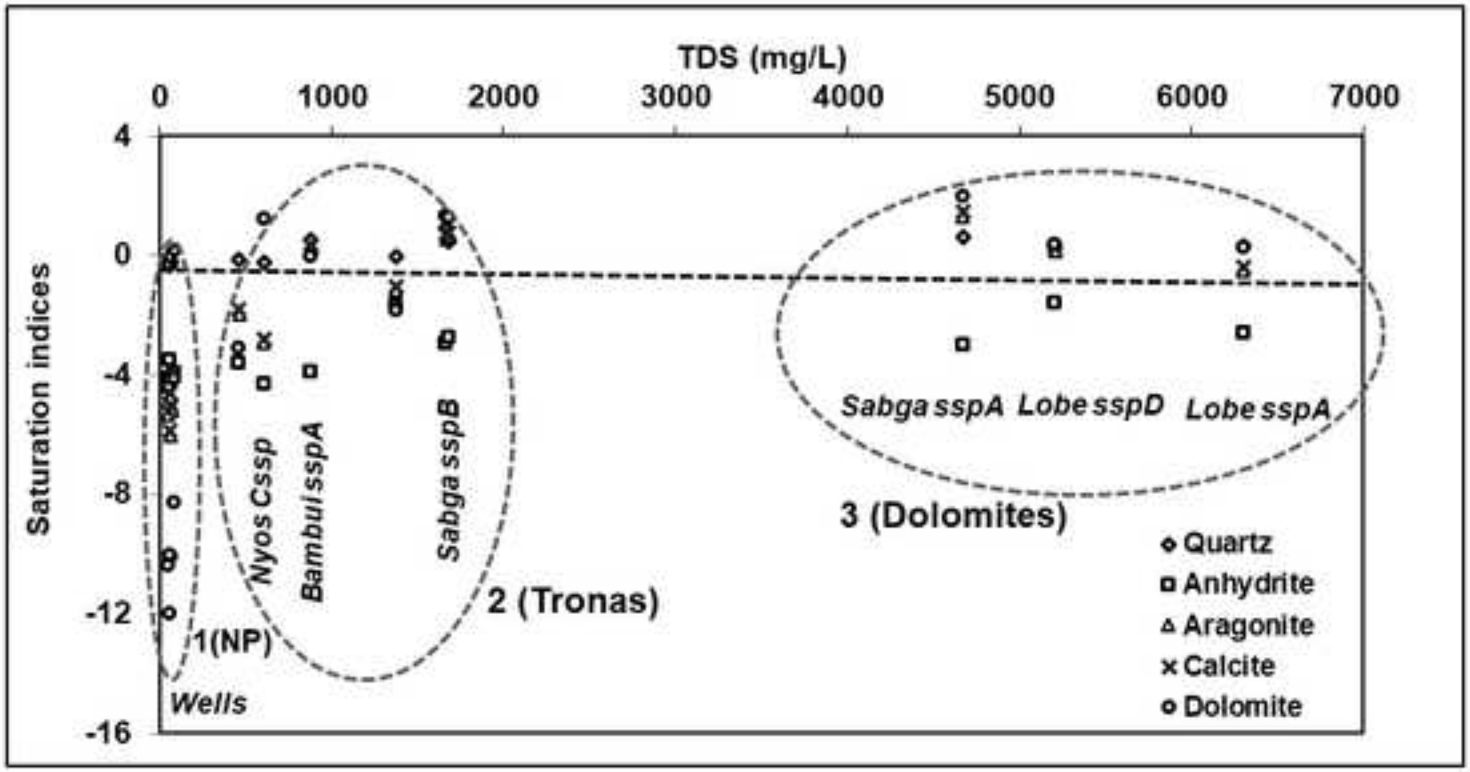

Figure 8

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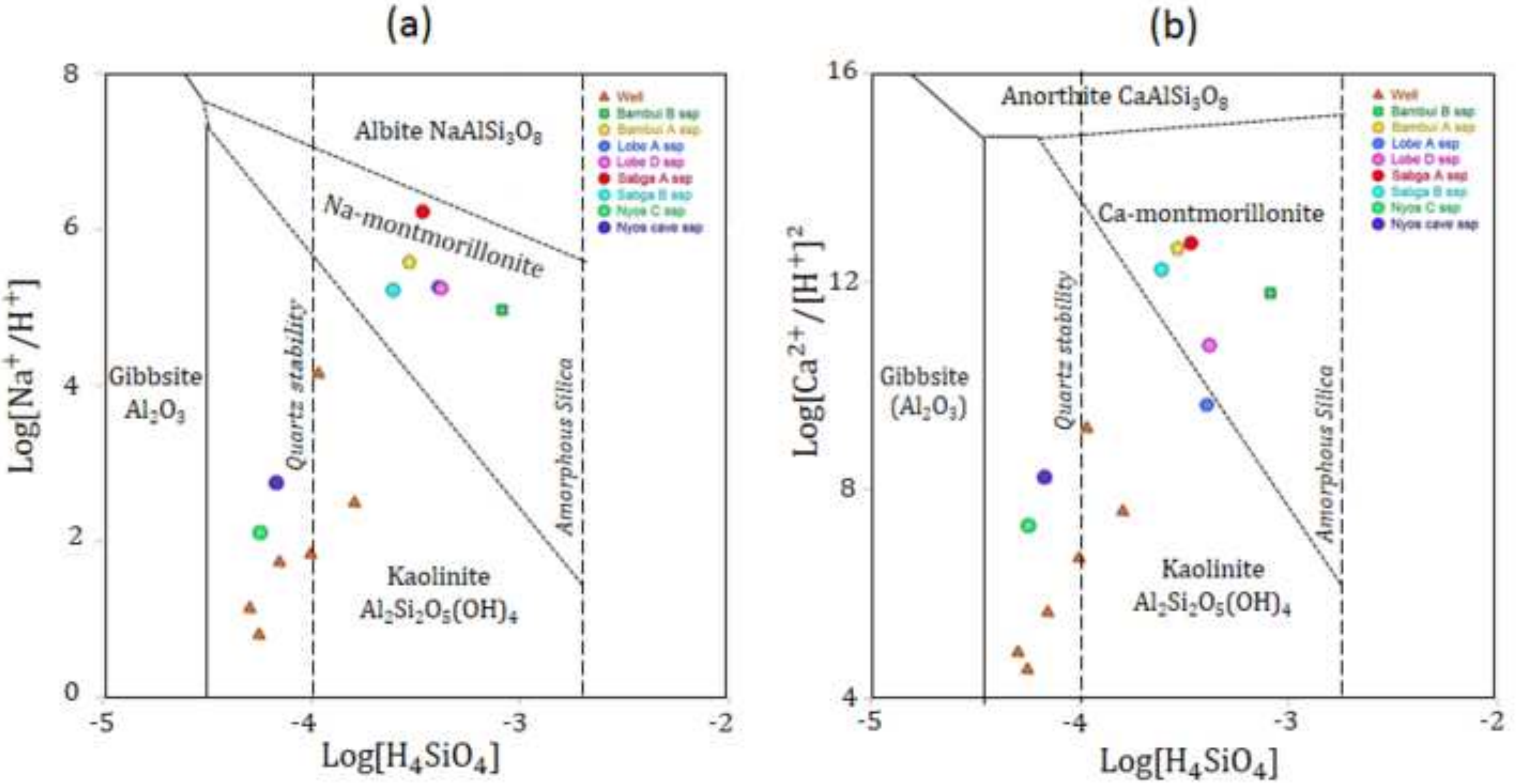
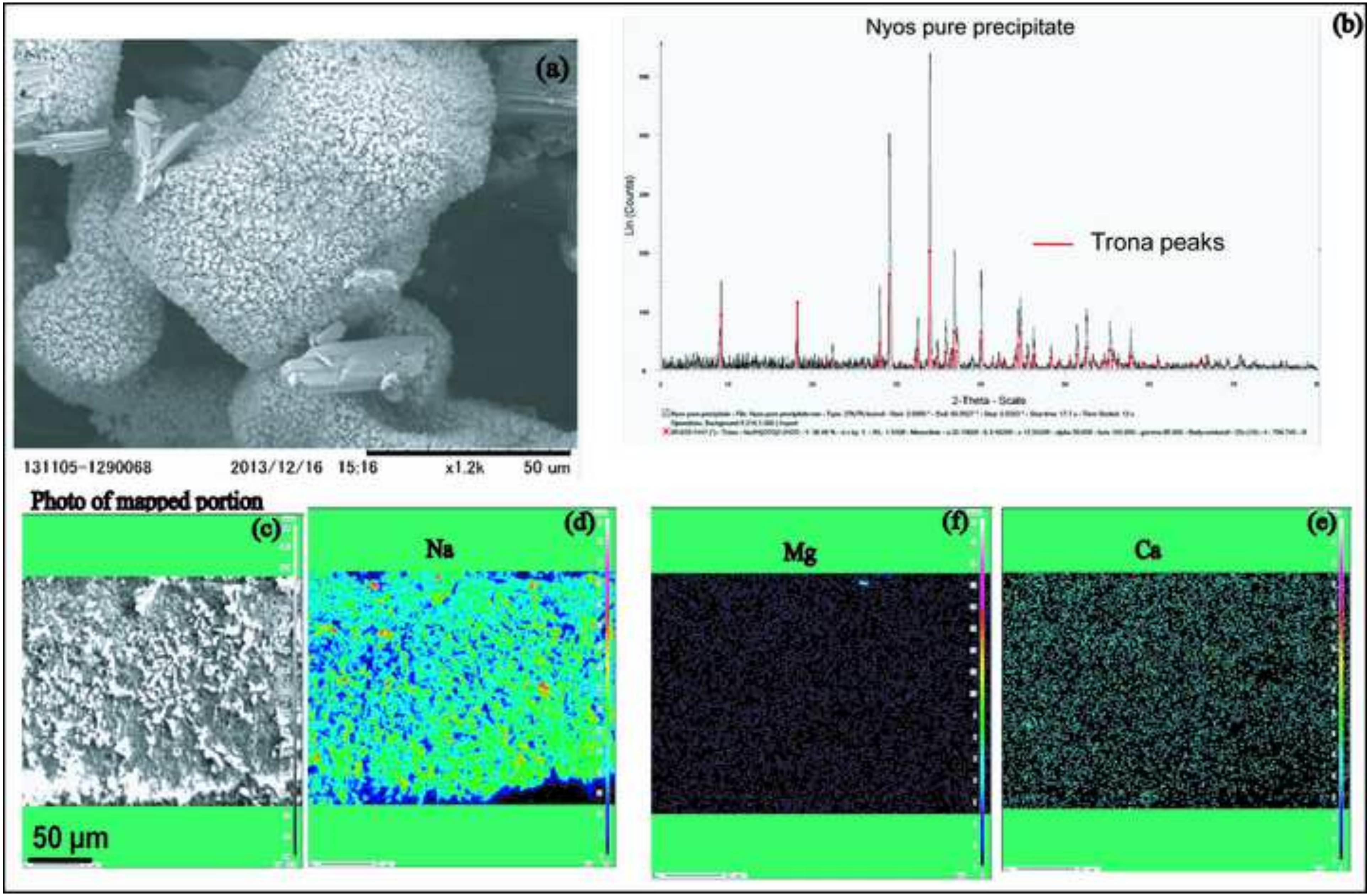


Figure 9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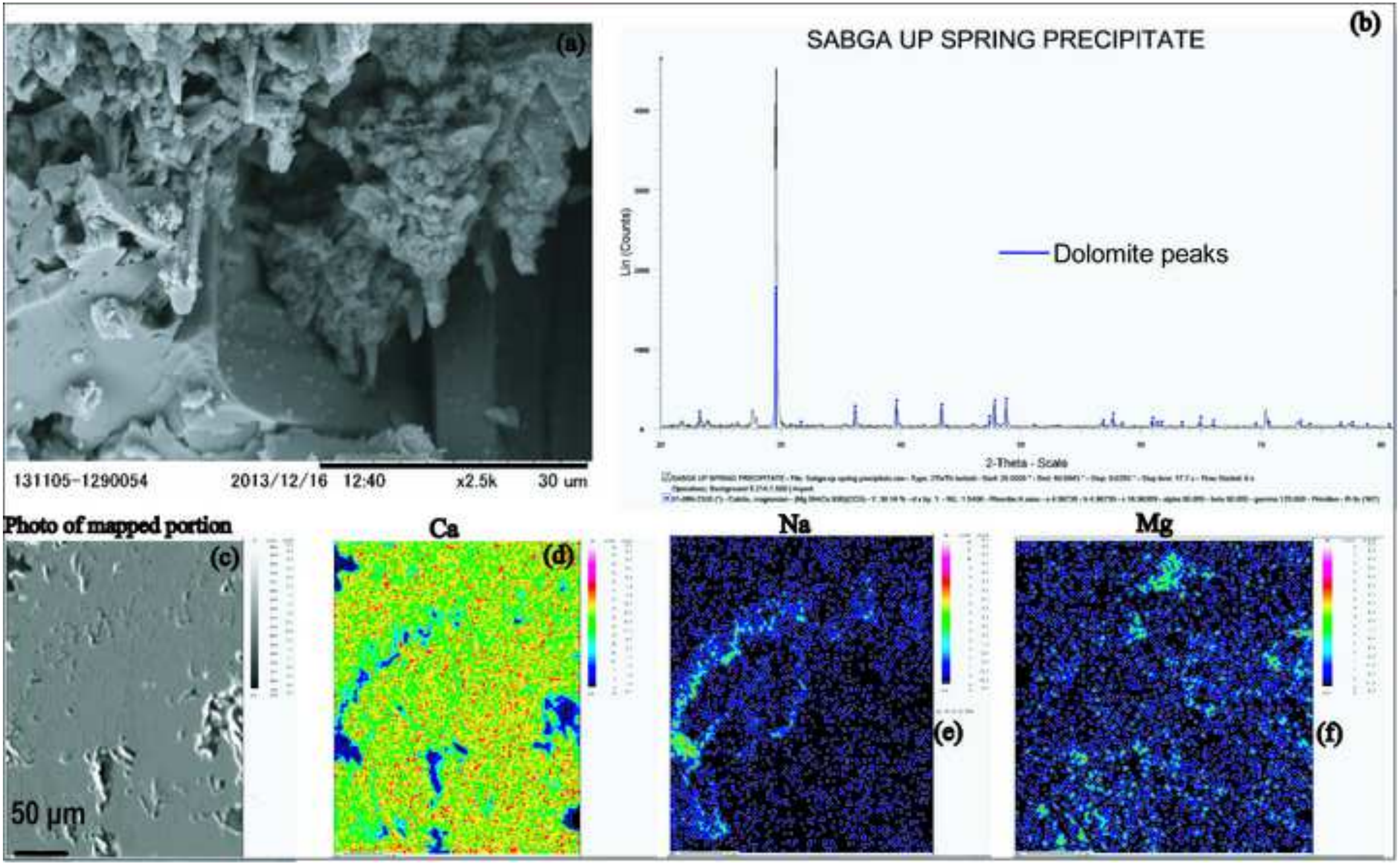
Trona peaks
Photo of mapped portion
(c)
50 µm
Na
(d)
Mg
(f)
Ca
(e)

Figure 10


(a)
131105-1290054
2013/12/16 12:40
x2.5k
30 um
(b)
SABGA UP SPRING PRECIPITATE
Lin (Counts)
Dolomite peaks
2-Theta - Scale
Photo of mapped portion
(c)
50 µm
Ca
(d)
Na
(e)
Mg
(f)

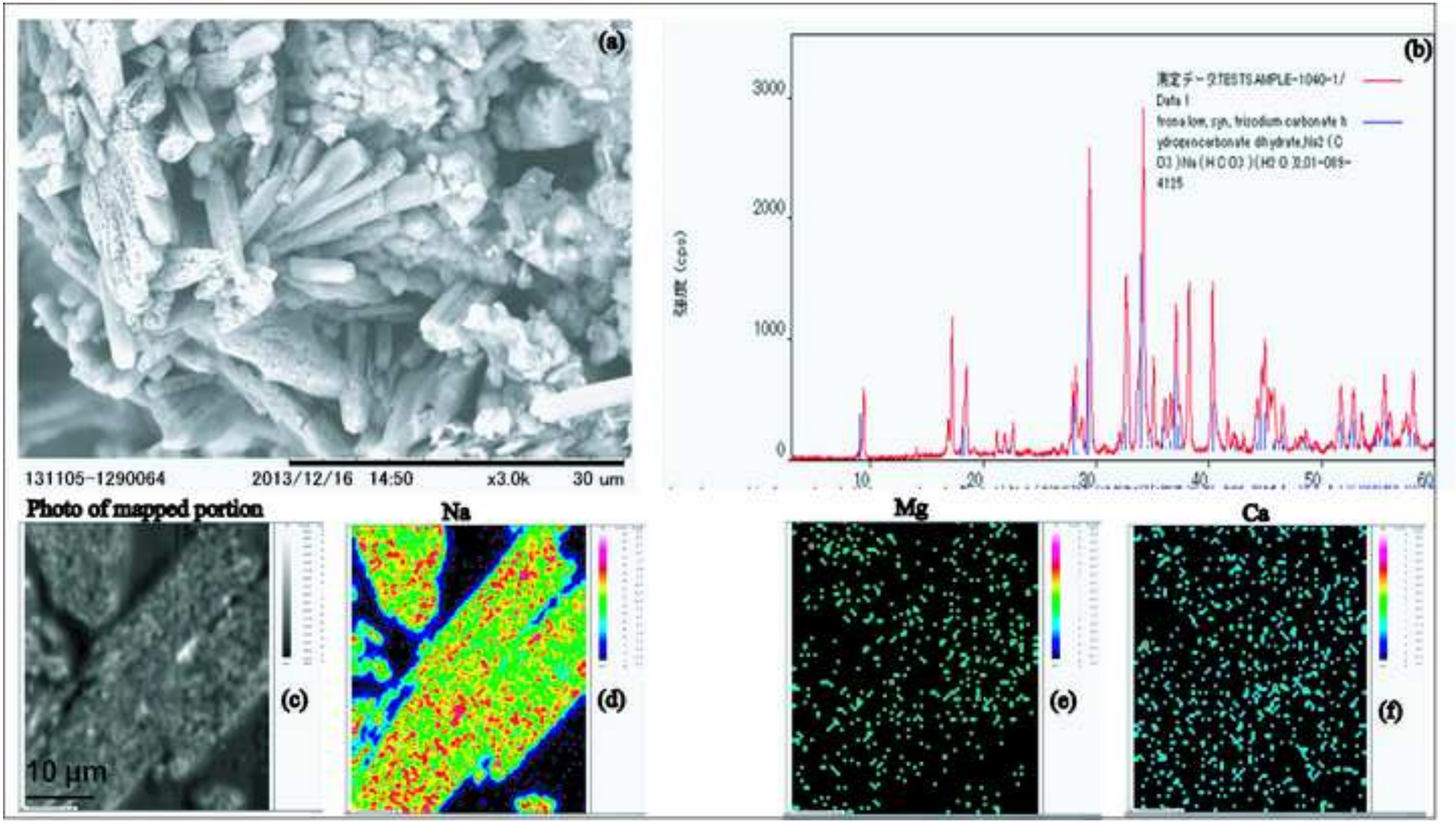

(a)
131105-1290064
2013/12/16 14:50
x3.0k
30 um
(b)
測定データ:TESTSAMPLE-1040-1/
Data 1
trona low, syn, trisodium carbonate h
ydrogencarbonate dihydrate,Na3 (C
O3)Na (H C O3)(H2 O)2,01-089-
4125
強度 (cps)
3000
2000
1000
0
10
20
30
40
50
60
Photo of mapped portion
10 µm
(c)
Na
(d)
Mg
(e)
Ca
(f)

Figure 12

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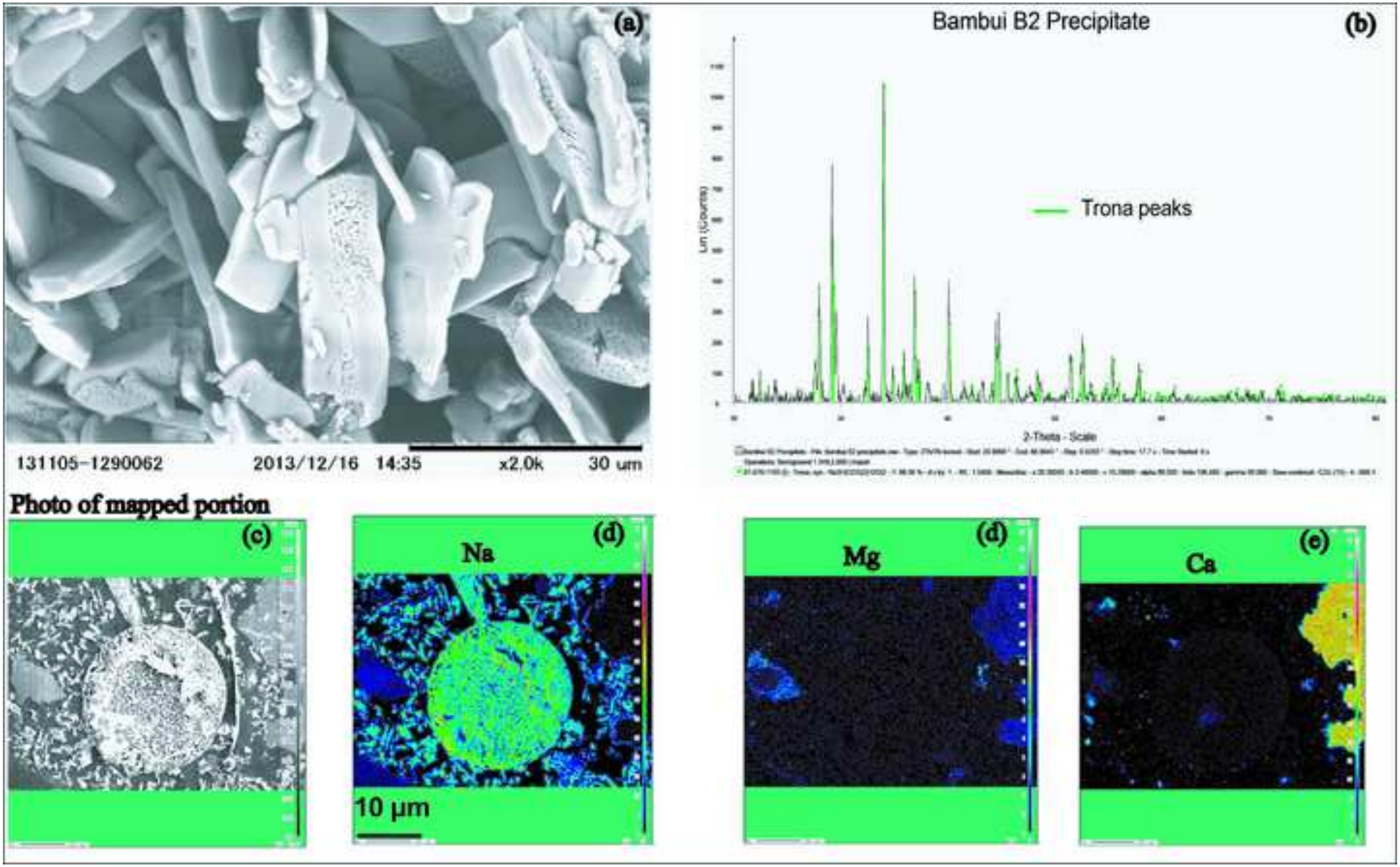

Figure 13

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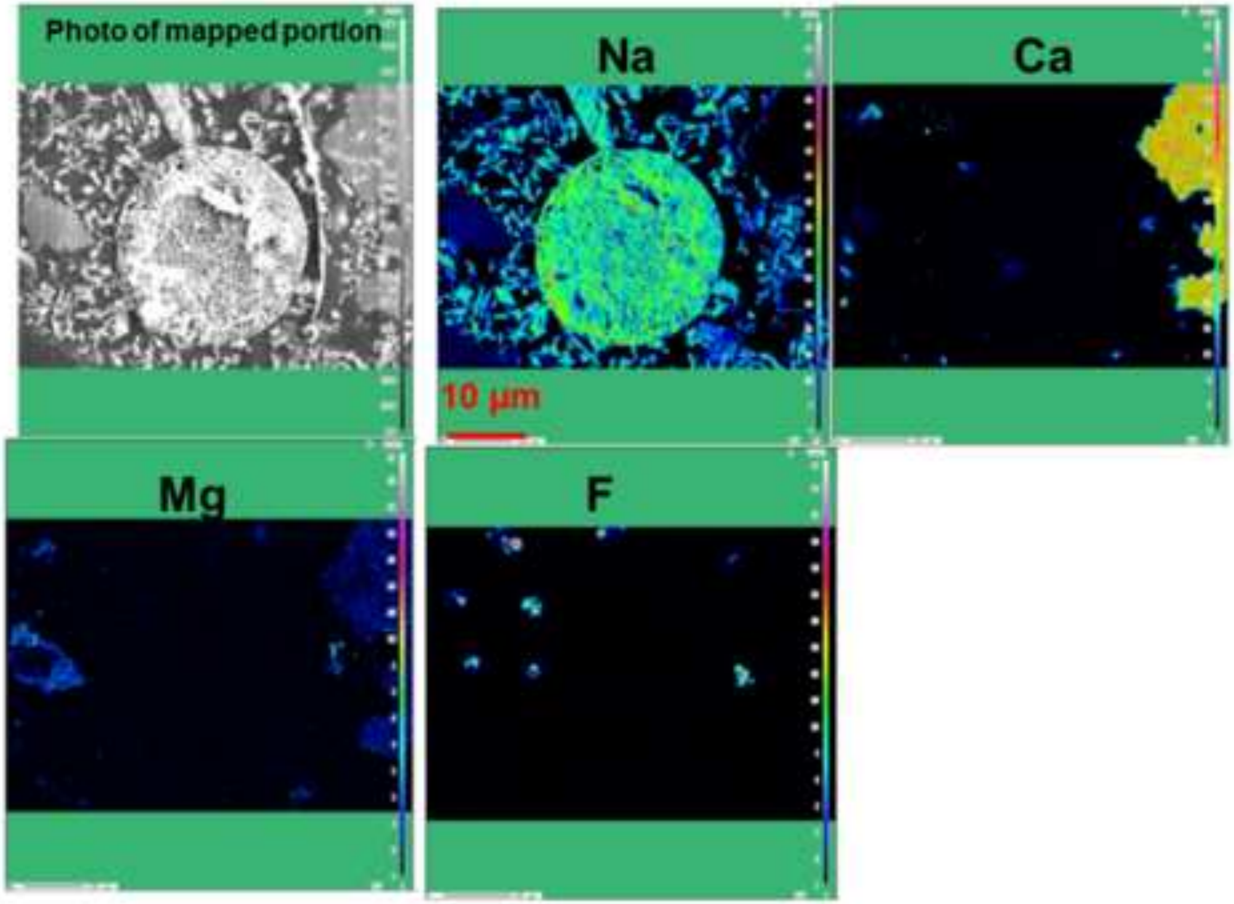

Figure 14

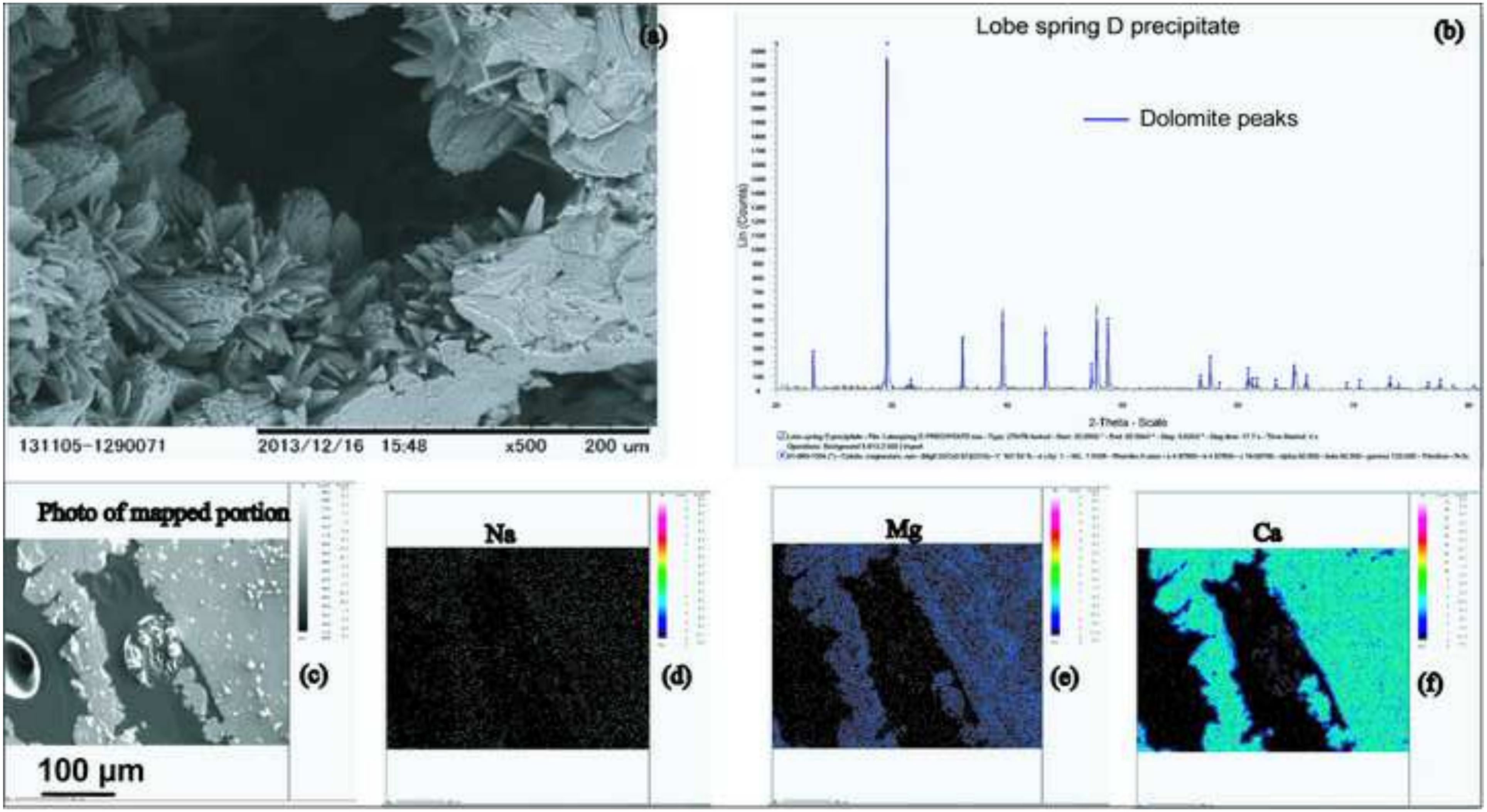
(a)
131105-1290071
2013/12/16 15:48
x500
200 um
Lobe spring D precipitate
(b)
Dolomite peaks
Lin (Counts)
2-Theta - Scale
Photo of mapped portion
(c)
100 µm
Na
(d)
Mg
(e)
Ca
(f)

Figure 15

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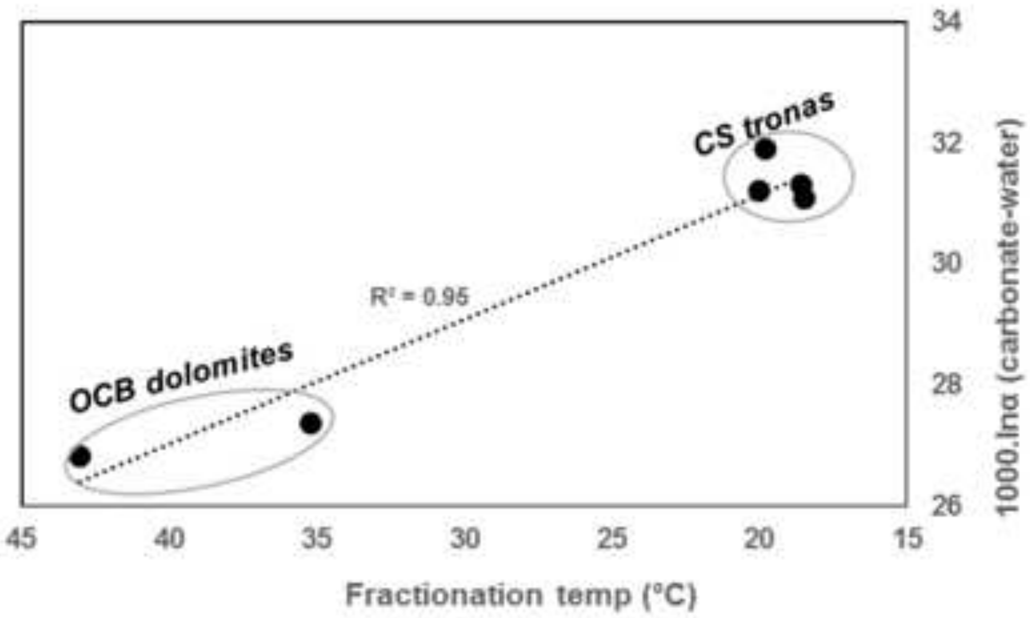

Figure 16

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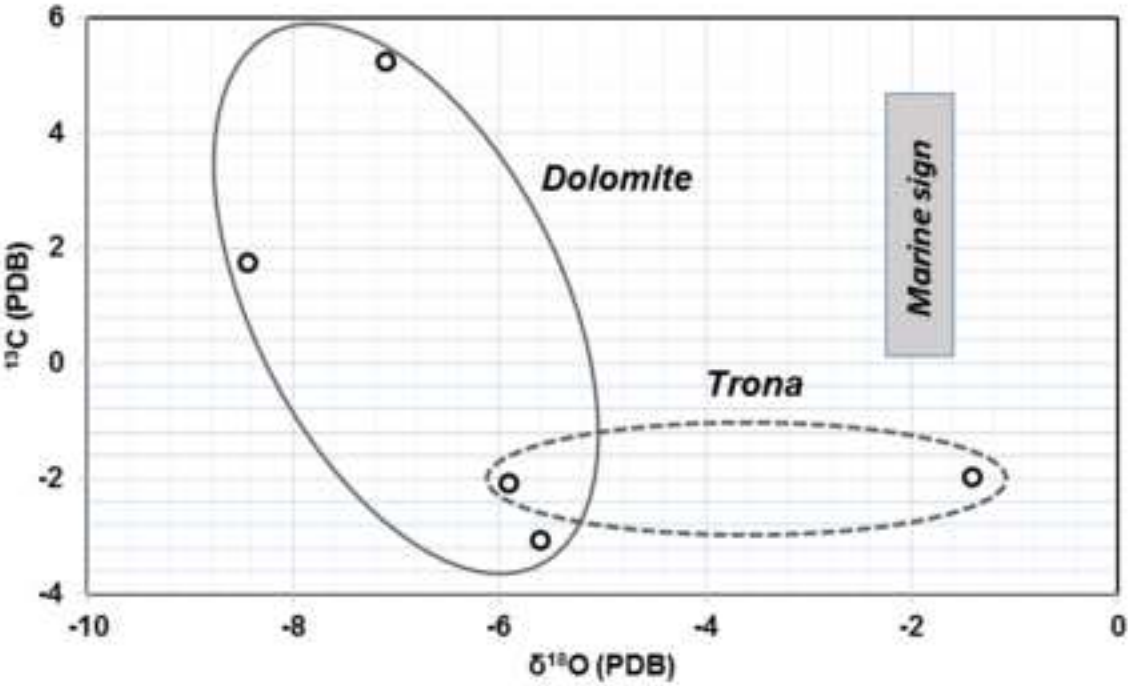

Figure 17a

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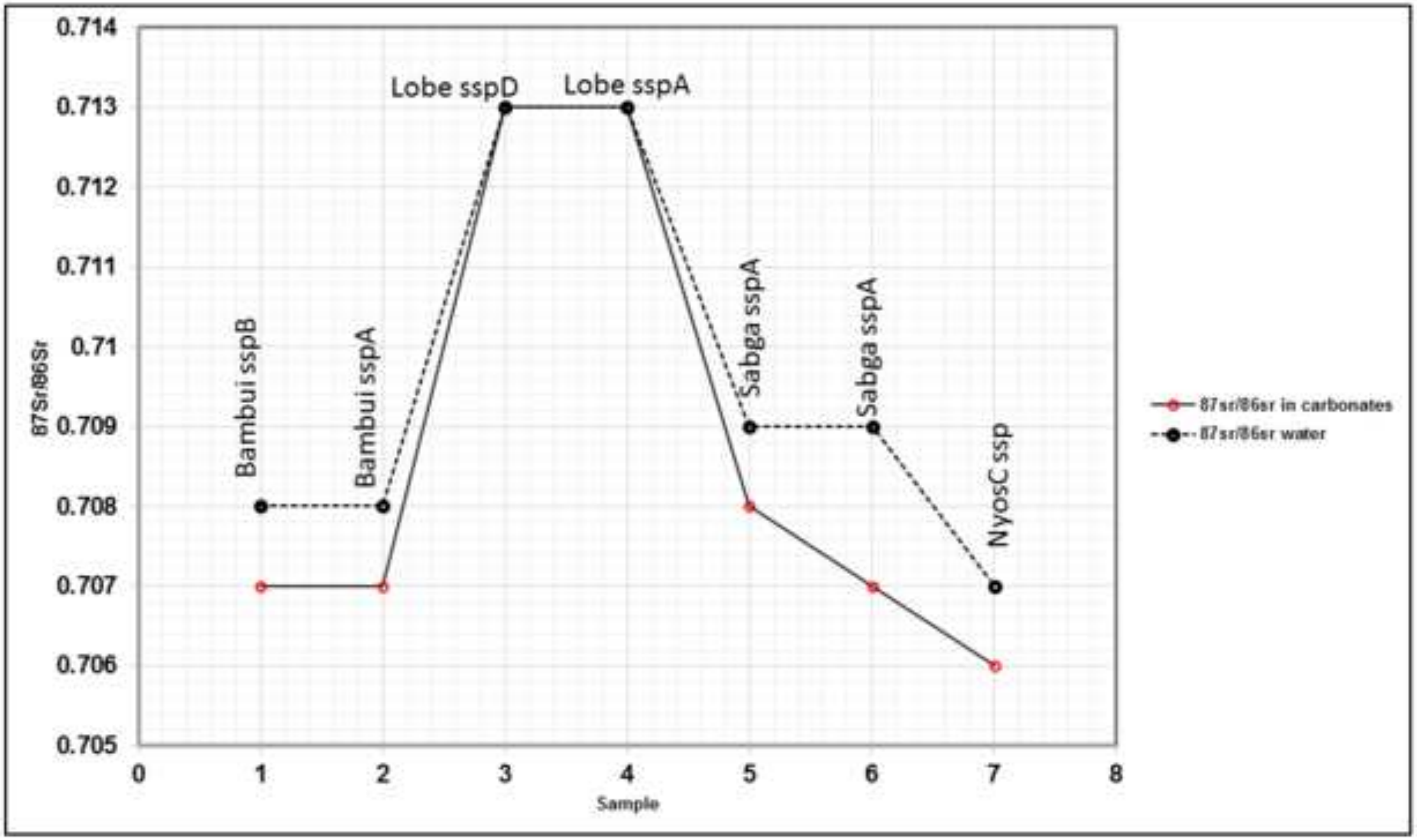

Figure 17b

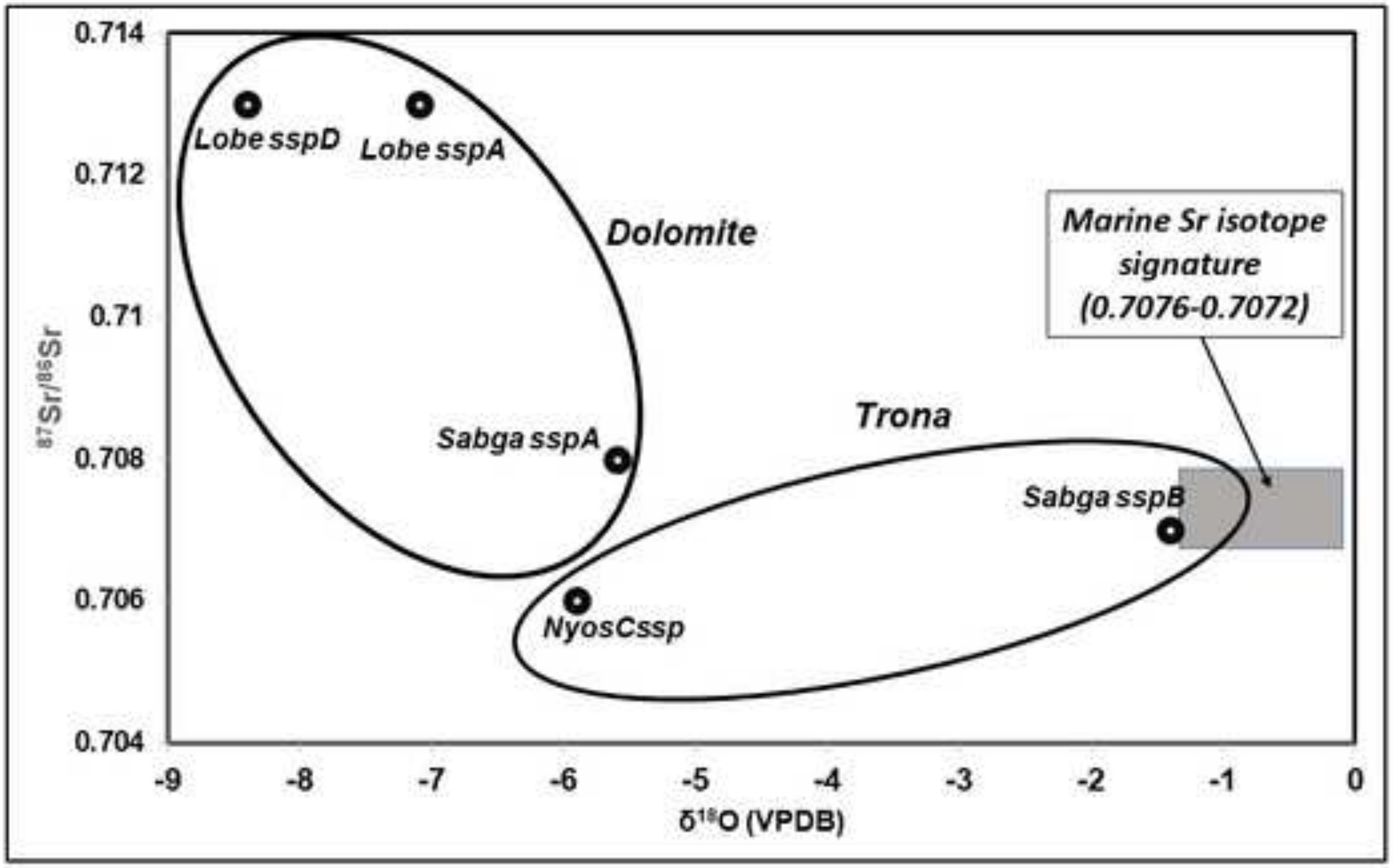
0.714
0.712
0.71
0.708
0.706
0.704
$^{87}Sr/^{86}Sr$
-9
-8
-7
-6
-5
-4
-3
-2
-1
0
$\delta^{18}O$ (VPDB)
Lobe sspD
Lobe sspA
Dolomite
Sabga sspA
Trona
NyosCssp
Sabga sspB
Marine Sr isotope signature (0.7076-0.7072)

Figure 18 Revised

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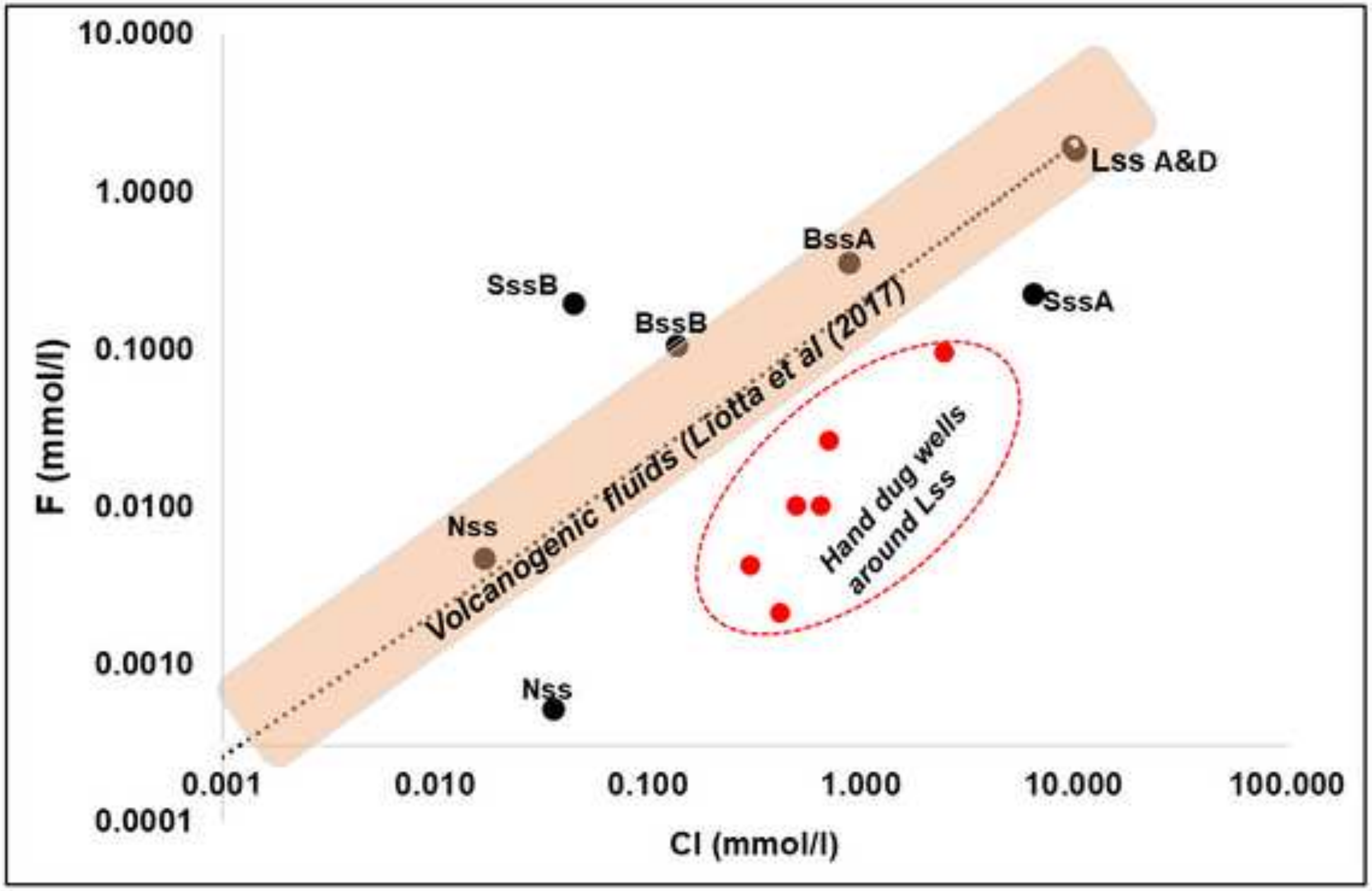

***Title page**

Major ions, $\delta^{18}O$, $\delta^{13}C$ and $^{87}Sr/^{86}Sr$ compositions of water and precipitates from springs along the Cameroon Volcanic Line (Cameroon, West Africa): Implications for provenance and volcanic hazards

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