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RESEARCH ARTICLE

DETERMINATION OF CHEMICAL COMPOSITION OF CAVE WATER: A CASE STUDY OF ZANZIBAR ISLAND, TANZANIA

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ABSTRACT

This study was carried out to determine the chemical composition of cave water in Zanzibar Island, part of Tanzania. It was done by studying major cations (Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}), and major anions (HCO_3^-, SO_4^{2-}, Cl^-), in the water as indicators. Overall results indicated that, the cave water was influenced by marine and weathering contribution. However, weathering was more pronounced at Chomvi ndogo, Chomvi kubwa, and Miza wa Miza caves where it was more than 87% compared to Kilindi, Choweni and Makutani caves where it was less than 77%. Therefore marine contributed more in these last three caves. The trend for concentration contributed from marine water was similar to all sampling sites which was K<Ca<Mg<SO_4<Na. The trend for weathering contribution was SO_4< K Mg<Na<Ca at Chomvi ndogo, Chomvi kubwa and Miza wa Miza caves while at Kilindi, Choweni and Makutani caves the trend was Mg<K <SO_4 <Na <Ca. These trends show that Na contributed more in marinogenic content in all caves while weathering contributed more by Calcium (Ca) in all sampling sites. PHREEQ program for saturation indices showed that, the major elements are supersaturated with calcite and aragonite and under saturated with anhydrite, gypsum, and quartz in all six caves.

INTRODUCTION

It is very important to study chemical composition at each cave so as to understand the relationship of that cave and water quality and make interpretations to the existing chemistry on specific site. For instance, cave waters respond to variations in surface recharge via changes in discharge and chemistry (Fairchild *et al*., 1996; Bar-Mathews *et al*., 1996; Baker *et al*., 2000; Huang *et al*., 2001; Frisia *et al*., 2003; Musgrove and Banner, 2004; Cruz *et al*., 2005). Such changes may be encoded in the chemical and physical properties of the speleothems deposited from these waters, allowing the extraction of palaeohydrological and other climate-related information (McDonald *et al*., 2007). According to Musgrove and Banner (2004) variations in isotopes and trace elements (Mg/Ca and Sr/Ca ratios) of waters and soils from different caves, as well as phreatic ground waters, provide the potential to distinguish between local variability and regional processes controlling fluid geochemistry, and a frame work for understanding the links between climatic and hydrologic processes. In this regard, chemical composition of cave water can vary, depending on the nature of the caves, rocks or soil, as well as weathering process taking place at the particular site. Stalagmite trace element concentration profiles can reveal evidence for climatic events that disrupt the local hydrological cycle (Baldini *et al*., 2006). Therefore, this study aimed to find out the chemical composition of cave water from caves in Zanzibar Island. First, it was to determine the chemical weathering taking place at each cave and influence of the tides to the water. Then marinogenic and non-marinogenic concentrations contributed to the cave water were calculated. Finally, PHREEQ geochemical program was used to identify the kind of minerals responsible for weathering process in each cave.

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Study area

Geography

This study was conducted in Zanzibar Island, Tanzania located in the Indian Ocean at Longitude 39° east and Latitude of 6° south of the equator (Else 1998). The study was on six different sites, two from each region of Zanzibar Island. The Chomvi ndogo, and Chomvi kubwa, are situated at Dimani, Urban – West region of Zanzibar. The Miza wa Miza and Kilindi from Kizimkazi, are caves from the Southern region of Zanzibar. The Choweni and Makutani are caves at Fukuchani, from the Northern region of Zanzibar (Fig. 1).

Figure for Zanzibar map showing Dimani, Fukuchani, and Kizimkazi and location of the caves where samples were taken for this study

MATERIAL AND METHODS

Water samples were taken from the six caves. Each cave was sampled twice in a day according to the sea tides. The first day of sampling was Sunday 14th December, 2008 during Lowest of the Low tidal (LL) at 11:10 AM when the tide frequency was 0.09 m and during Highest of the High tidal (HH) at 5:15 PM when the tide frequency was 3.46 m. The second sampling day was Monday 22nd December, 2008 at 6:47 AM and 12:28 PM when the tides frequencies were 1.38 m and 2.56 m for Highest of the Low tidal (HL) and Lowest of the High tidal (LH) respectively. Water samples were taken in plastic bottles and were kept in cooling container to the laboratory for analysis. The samples after collected were filtered through 0.45µm cellulose-acetate filter membrane to remove total suspended particles. Each sample was then divided into two portions of 500mls each. The first portion was for anion analysis, and the second portion for cation analysis. The portion for cation analysis was preserved by adding 3mls of conc. HCl while for anion was preserved by freezing at -4 ^{0}C (Clesceri *et al*., 1998). The cations Na^+, K^+, Ca^{2+}, and Mg^{2+} were analyzed using the Induced Coupling Plasma Mass Spectrophotometer, ICP-MS (X-7, Thermo Elemental) at the Southern and Eastern African Mineral Centre, Kunduchi Dar es Salaam, Tanzania. Sulphate was measured by Turbid metric method, Bicarbonate alkalinity was analyzed by titration against 0.05M HCl using Methyl Orange as indicator. Chloride was analyzed by titration against 0.05M $AgNO_3$ by using potassium chromate as indicator (Clesceri *et al*., 1998). Analysis for anions was done at Ardhi

University laboratory situated at Mwenge, Dar es Salaam Tanzania.

Sources of major chemical species

With exception of the values from Chomvi ndogo only, the total dissolved cations (TC) and total dissolved anions (TA) were balanced to within $\pm 9.9\%$ of the normalized inorganic charge balance (NICB) (Table 2) and show the linear relation with slope of 1.0943 and R square value of 0.9669 (Fig.1). The total cations (TC), total anions (TA), and normalized organic charge balance (NICB) were calculated using the following formulas;

TC (Total Dissolved Cations) = $Na^+ + K^+ + 2Mg^{2+} + 2Ca^{2+}$

TA (Total Dissolved Anions) = $Cl^- + HCO_3^- + 2SO_4^{2-}$

NICB (Normalized Inorganic Charge Balance) = (TC – TA)/TC x 100

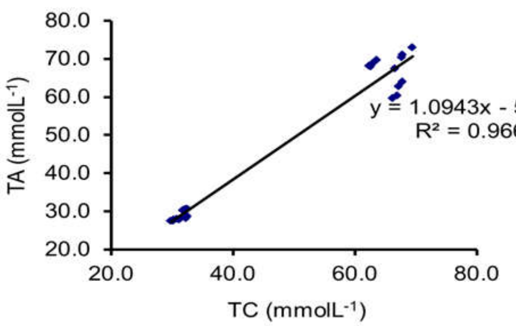

Figure 1: Relationship between total cations (TC) and total anions (TA) in mmol^{-1}

Chemical species in ground water, cave being one of the types, may originate either from marine or rock weathering. This was tested by inter-species relationship and the results were presented in table 3. The samples showed strong correlations (P<0.05) among cations and anions for all concentrations. The correlations emphasize the importance of both marine and weathering species. Concentration of Ca^{2+} showed strong correlation with SO_4^{2-} and HCO_3^- indicating existence of $Ca(HCO_3)_2$ and $CaSO_4$ (Vuai, 2004). The existence of $Ca(HCO_3)_2$ may be responsible for the high pH observed in this study, whereas $CaSO_4$ is associated with dissolution of gypsum mineral. The relationship between Na^+ and Cl^- (fig. 3) was very strong indicating the common sources of these species, since the slope was 0.9959 which is very close to one.

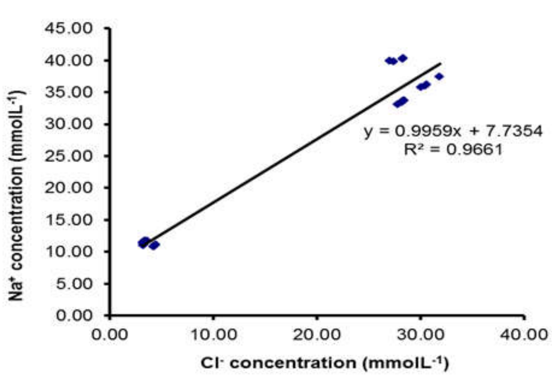

Figure 2: Relationship between Sodium and Chloride concentrations

Chloride is the major component of sea water which contributes about 19,350 mgL^{-1} or 540mmolL^{-1}. The chloride concentration was used to understand the relationship between marinogenic and non marinogenic species, which were obtained by the following relation:-

$$Ci_{marine} = \frac{C_{Cl-cavewater}}{C_{Cl-seawater}} \text{ x } Ci_{seawater}$$

Where;

Ci_{marine} = Concentration of chemical species contributed to marine

$Ci_{seawater}$ = Concentration of chemical species in sea water

$C_{Cl-cavewater}$ = Concentration of Cl^- from cave water

$C_{Cl-seawater}$ = Concentration of Cl^- in sea water

The sea water concentrations used in calculation is shown in table 4

The concentration of non marinogenic (weathering) was obtained by subtracting the concentration of chemical species found in the sample with that contributed by the sea water. The percentages for both marinogenic and weathering were then calculated and presented in the table 5.

The major elements composition indicates that weathering was important at Chomvi ndogo, Chomvi kubwa and Miza wa Miza caves compared to rest of other caves. In this regard the total salt contribution was very low (less than 13%) in these caves. Therefore the weathering contribution in these caves was more than 87%. However in Kilindi, Choweni and Makutani caves show reverse trend, because the salt water contribution was very high to these caves. The total value of salt contribution in these caves was greater than 33%. These trends confirm that the tides have significant effect at Kilindi, Makutani and Choweni caves since they receive large amount of salt water which was truly come from the oceans while Chomvi kubwa, Chomvi ndogo, and Miza wa Miza cave, tides show less effect (Fig.3). The trend for concentration contributed from marine water was similar to all sampling sites which was K<Ca<Mg<SO_4<Na. The trend for weathering contribution was SO_4< K Mg<Na<Ca at Chomvi ndogo, Chomvi kubwa and Miza wa Miza caves while Kilindi, Choweni and Makutani the trend was Mg<K <SO_4 <Na <Ca (Table 5). These trends show that Na contribute more in maringenic content in all caves while weathering is contributed more by Calcium (Ca) in all sampling sites (Table 5). Vuai and Tokuyama (2007) found Calcium was more weathered than other element. Therefore the trend in this study was agreed with their results for all caves.

Possible mineral for weathering

The possible minerals responsible for releasing those species in cave water are presented in table 6. In soil water and ground water where carbonic acid concentration is high, the resulting concentrations of Ca^{2+} and HCO^-_3 can build up to high values. This can be achieved in the presence of carbonate minerals through the equations such and fig.3 below:-

Calcite dissolution

$$H_2CO_3 + CaCO_3 \rightarrow Ca^{2+} + 2HCO_3^-$$
(Calcite)

Table 1: Table of results

SITE	DATE	TIDE	Ca^{2+} (mgL^{-1})	Mg^{2+} (mgL^{-1})	Na^{+} (mgL^{-1})	K^{+} (mgL^{-1})	$HCO3^{-}$ (mgL^{-1})	$SO4^{2-}$ (mgL^{-1})	Cl^{-} (mgL^{-1})
CN	14/12/08	HH	652 ± 15.4	47.6 ± 3.04	271 ± 5.97	20.8 ± 6.38	1496 ± 32.7	31.0 ± 1.41	128 ± 2.12
CN	14/12/08	LL	649 ± 13.6	43.2 ± 2.08	256 ± 12.6	18.2 ± 5.87	1489 ± 27.1	24.5 ± 2.12	116 ± 5.80
CN	22/12/08	LH	648 ± 7.91	38.0 ± 7.35	254 ± 17.0	27.2 ± 8.53	1471 ± 26.2	20.0 ± 2.83	115 ± 5.47
CN	22/12/08	HL	651 ± 6.00	43.2 ± 4.45	267 ± 0.78	30.6 ± 4.84	1485 ± 37.6	23.0 ± 4.24	122 ± 3.13
CK	14/12/08	HH	616 ± 17.1	36.5 ± 2.55	270 ± 14.9	23.0 ± 3.71	1471 ± 30.4	22.5 ± 2.12	120 ± 3.31
CK	14/12/08	LL	610 ± 17.1	34.2 ± 3.35	265 ± 14.0	21.2 ± 4.33	1457 ± 27.6	18.5 ± 4.95	115 ± 4.41
CK	22/12/08	LH	609 ± 8.50	32.1 ± 2.15	261 ± 12.8	21.1 ± 3.45	1455 ± 20.6	16.5 ± 0.71	115 ± 7.18
CK	22/12/08	HL	611 ± 11.5	35.9 ± 2.25	262 ± 6.53	22.8 ± 4.26	1468 ± 24.6	25.0 ± 1.41	115 ± 3.72
MM	14/12/08	HH	697 ± 23.3	37.3 ± 4.04	255 ± 4.04	36.9 ± 5.03	1554 ± 21.8	33.5 ± 2.12	158 ± 4.11
MM	14/12/08	LL	695 ± 19.6	34.9 ± 0.71	250 ± 8.32	33.9 ± 5.15	1550 ± 13.9	29.5 ± 0.71	154 ± 4.14
MM	22/12/08	LH	694 ± 13.0	33.1 ± 4.74	249 ± 4.29	32.8 ± 5.02	1548 ± 7.69	27.0 ± 1.41	152 ± 6.62
MM	22/12/08	HL	695 ± 25.4	36.5 ± 2.67	254 ± 1.03	34.3 ± 6.73	1562 ± 30.0	27.5 ± 3.54	154 ± 3.99
KL	14/12/08	HH	774 ± 27.4	81.1 ± 10.7	928 ± 11.1	51.4 ± 5.69	1559 ± 31.6	480 ± 4.95	1008 ± 3.17
KL	14/12/08	LL	767 ± 44.8	80.5 ± 14.5	917 ± 15.6	49.7 ± 4.65	1554 ± 21.7	361 ± 4.95	973 ± 5.91
KL	22/12/08	LH	764 ± 61.2	70.4 ± 17.8	919 ± 15.3	49.9 ± 5.52	1557 ± 28.3	340 ± 1.41	959 ± 26.7
KL	22/12/08	HL	771 ± 31.5	76.9 ± 14.0	925 ± 10.5	50.5 ± 5.23	1568 ± 17.7	420 ± 3.54	1004 ± 8.72
CW	14/12/08	HH	891 ± 11.5	95.6 ± 10.1	861 ± 16.7	70.7 ± 12.7	1791 ± 11.4	565 ± 4.24	1132 ± 6.23
CW	14/12/08	LL	887 ± 5.39	92.8 ± 10.2	828 ± 15.5	73.7 ± 1.74	1778 ± 14.7	550 ± 6.36	1082 ± 1.79
CW	22/12/08	LH	866 ± 9.33	87.2 ± 7.91	822 ± 19.0	74.0 ± 6.73	1736 ± 27.3	425 ± 3.54	1067 ± 8.02
CW	22/12/08	HL	880 ± 21.3	90.3 ± 5.77	833 ± 28.0	75.6 ± 1.07	1788 ± 12.1	500 ± 5.66	1086 ± 19.5
MK	14/12/08	HH	851 ± 10.2	78.3 ± 12.4	776 ± 18.6	78.9 ± 3.32	1692 ± 12.5	651 ± 2.12	1009 ± 4.36
MK	14/12/08	LL	832 ± 13.3	78.0 ± 16.0	760 ± 32.6	76.5 ± 4.37	1671 ± 17.8	620 ± 4.95	987 ± 19.0
MK	22/12/08	LH	833 ± 24.6	78.0 ± 14.8	767 ± 6.12	75.2 ± 4.47	1663 ± 40.5	600 ± 3.54	1000 ± 8.11
MK	22/12/08	HL	834 ± 3.31	78.2 ± 13.1	772 ± 22.3	77.5 ± 3.68	1668 ± 2.25	630 ± 2.83	1004 ± 6.37

NOTE: CN = Chomvi ndogo, CK = Chomvi kubwa, MM = Miza wa Miza, KL = Kilindi, CW = Choweni and MK = Makutani

Table 2: Dissolved chemical species in cave water ($mmolL^{-1}$) and the ratios of total cations with total anions calculated from the main data

SITE	DATE	TIDE	Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}	HCO_3^{-}	SO_4^{2-}	Cl^{-}	TC	TA	%NICB	TC/TA
CN	081214	HH	16.3	3.96	11.8	0.53	24.5	0.65	3.60	32.6	28.8	11.6	1.13
CN	081214	LL	16.2	3.60	11.1	0.47	24.4	0.50	3.27	31.4	28.2	10.3	1.11
CN	081222	LH	16.2	3.17	11.0	0.70	24.1	0.42	3.25	31.1	27.8	10.7	1.12
CN	081222	HL	16.3	3.60	11.6	0.78	24.3	0.48	3.43	32.3	28.3	12.4	1.14
CK	081214	HH	15.4	3.04	11.7	0.59	24.1	0.46	3.37	30.8	27.9	9.16	1.10
CK	081214	LL	15.3	2.85	11.5	0.54	23.9	0.40	3.23	30.2	27.5	8.79	1.10
CK	081222	LH	15.2	2.68	11.3	0.54	23.8	0.35	3.25	29.8	27.5	7.82	1.08
CK	081222	HL	15.3	2.99	11.4	0.58	24.1	0.52	3.23	30.3	27.8	8.08	1.09
MM	081214	HH	17.4	3.10	11.1	0.95	25.5	0.69	4.45	32.6	30.6	6.03	1.06
MM	081214	LL	17.4	2.91	10.9	0.87	25.4	0.60	4.33	32.0	30.3	5.27	1.06
MM	081222	LH	17.3	2.76	10.8	0.84	25.4	0.56	4.27	31.7	30.2	4.87	1.05
MM	081222	HL	17.4	3.04	11.0	0.88	25.6	0.58	4.32	32.3	30.5	5.58	1.06
KL	081214	HH	19.4	6.75	40.4	1.32	25.6	10.0	28.4	67.8	64.0	5.65	1.06
KL	081214	LL	19.2	6.71	39.9	1.27	25.5	7.50	27.4	67.0	60.4	9.88	1.11
KL	081222	LH	19.1	5.87	40.0	1.28	25.5	7.08	27.0	66.2	59.6	9.94	1.11
KL	081222	HL	19.3	6.41	40.2	1.29	25.7	8.75	28.3	67.2	62.7	6.63	1.07
CW	081214	HH	22.3	7.97	37.4	1.81	29.4	11.8	31.9	69.5	73.0	-5.08	0.95
CW	081214	LL	22.2	7.73	36.0	1.89	29.1	11.5	30.5	67.8	71.1	-4.85	0.95
CW	081222	LH	21.6	7.27	35.7	1.90	28.5	8.85	30.1	66.6	67.4	-1.23	0.99
CW	081222	HL	22.0	7.53	36.2	1.94	29.3	10.4	30.6	67.7	70.3	-3.89	0.96
MK	081214	HH	21.3	6.52	33.7	2.02	27.7	13.5	28.4	63.6	69.7	-9.64	0.91
MK	081214	LL	20.8	6.50	33.1	1.96	27.4	12.9	27.8	62.3	68.1	-9.30	0.91
MK	081222	LH	20.8	6.50	33.4	1.93	27.3	12.5	28.2	62.6	67.9	-8.51	0.92
MK	081222	HL	20.8	6.51	33.6	1.99	27.3	13.1	28.3	62.9	68.7	-9.25	0.92

Table 3: Correlation coefficients of concentrations of major chemical species from cave water

	Na^+	K^+	Mg^{2+}	Ca^{2+}	HCO_3^-	Cl^-	SO_4^{2-}
Na^+	1.00						
K^+	0.70	1.00					
Mg^{2+}	0.91	0.81	1.00				
Ca^{2+}	0.74	0.94	0.88	1.00			
HCO_3^-	0.51	0.85	0.72	0.92	1.00		
Cl^-	0.97	0.84	0.96	0.87	0.67	1.00	
SO_4^{2-}	0.83	0.91	0.88	0.86	0.69	0.92	1.00

Table 4: Sea water concentrations of salinity 35% used for calculating the concentrations of marinogenic and weathering species in cave water

Constituent	mgL^{-1}	$mmolL^{-1}$
Sodium	10,760	468.0
Magnesium	1,294	53.2
Calcium	412	10.2
Potassium	399	10.2
Chloride	19,350	545.0
Sulphate	2,712	28.2

Table 5: Sea and weathering contribution in chemical species (mgL^{-1}) to the cave water of sampling sites

		Chomvi ndogo		Chomvi kubwa		Miza wa Miza		Kilindi		Choweni		Makutani	
Element	**Tide**	**Mc**	**Wc**	**Mc**	**Wc**	**Mc**	**Wc**	**Mc**	**Wc**	**Mc**	**Wc**	**Mc**	**Wc**
Calcium	HH	2.72	649	2.55	614	3.36	694	21.5	753	24.1	867	21.5	829
	LL	2.47	646	2.44	608	3.27	692	20.7	746	23.0	864	21.0	811
	LH	2.46	646	2.46	606	3.23	691	20.4	744	22.7	843	21.3	811
	HL	2.59	649	2.44	609	3.27	691	21.4	749	23.1	857	21.4	813
Magnesium	HH	8.55	39.0	7.99	28.5	10.6	26.7	67.4	13.6	75.7	20.0	67.4	10.8
	LL	7.77	35.4	7.66	26.5	10.3	24.6	65.0	15.4	72.4	20.4	66.0	12.0
	LH	7.72	30.3	7.71	24.4	10.1	23.0	64.1	6.3	71.4	15.8	66.9	11.1
	HL	8.15	35.0	7.67	28.2	10.3	26.2	67.1	9.7	72.6	17.7	67.1	11.0
Sodium	HH	71.1	200	66.5	203	3.25	33.6	561	367	629	232	561	215
	LL	64.6	191	63.7	201	3.17	30.8	541	376	602	226	549	211
	LH	64.2	190	64.1	197	3.12	29.7	533	386	593	229	556	211
	HL	67.8	199	63.8	199	3.16	31.1	558	367	604	229	558	214
Potassium	HH	2.63	18.1	2.46	20.5	3.25	33.6	20.8	30.7	23.3	47.4	20.8	58.1
	LL	2.39	15.8	2.36	18.8	3.17	30.8	20.0	29.6	22.3	51.4	20.3	56.2
	LH	2.38	24.8	2.38	18.7	3.12	29.7	19.8	30.1	22.0	52.0	20.6	54.6
	HL	2.51	28.1	2.36	20.4	3.16	31.1	20.7	29.8	22.4	53.2	20.7	56.8
Sulphate	HH	17.9	13.1	16.8	5.24	22.1	10.9	141	339	159	406	141	509
	LL	16.3	7.71	16.1	2.94	21.5	7.46	136	224	152	398	138	482
	LH	16.2	3.82	16.2	0.84	21.2	5.76	134	206	150	275	140	460
	HL	17.1	5.92	16.1	8.93	21.5	6.49	141	279	152	348	141	489
TOTAL	HH	103	919	96.2	871	127	932	812	1503	911	1572	812	1622
	LL	93.6	896	92.3	857	124	919	783	1390	871	1560	795	1572
	LH	92.9	894	92.8	847	122	913	772	1371	859	1415	805	1548
	HL	98.1	917	92.3	865	124	924	808	1435	874	1505	808	1584
%TOTAL	HH	10.1	89.9	9.95	90.1	12.0	88.0	35.1	64.9	36.7	63.3	33.4	66.6
	LL	9.45	90.5	9.72	90.3	11.9	88.1	36.0	64.0	35.8	64.2	33.6	66.4
	LH	9.41	90.6	9.88	90.1	11.8	88.2	36.0	64.0	37.8	62.2	34.2	65.8
	HL	9.67	90.3	9.64	90.4	11.8	88.2	36.0	64.0	36.7	63.3	33.8	66.2

Note: Mc = Marine contribution, Wc = Weathering contribution

Table 6: Some common minerals that undergo weathering, their composition and possible rock types

Mineral	Composition	Rock type
Calcite	$CaCO_3$	Sedimentary
Dolomite	$CaMg(CO_3)_2$	Sedimentary
Pyrite	FeS2	Sedimentary
Gypsum	$CaSO_4\ 2H_2O$	Sedimentary
Anhydrite	$CaSO_4$	Sedimentary
Plagioclase feldspar	$NaAlSi_3O_8$ (albite) CaAl $Si2O_8$ (anorthite)	Igneous Metamorphic
K-feldspar	$KAlSi_3O8$	Igneous Metamorphic Sedimentary
Biotite	$K(Mg,Fe)_3(AlSi_3O_{10})(OH)_2$	Metamorphic Igneous
Halite	NaCl	Sedimentary
Pyroxene	$Ca(Mg,Fe)Si_2O_6$ or $(Mg,Fe)SIO_3$	Igneous

Table 7: Saturation indices for different minerals as calculated from concentration of chemical species in cave water

MINERAL	TIDE	CHOMVI NDOGO	CHOMVI KUBWA	MIZA WA MIZA	KILINDI	CHOWENI	MAKUTANI
ANHYDRITE	HH	-1.89	-2.04	-1.84	-0.77	-0.68	-0.61
	LL	-1.99	-2.10	-1.90	-0.89	-0.69	-0.64
	LH	-2.07	-2.15	-1.92	-0.92	-0.80	-0.66
	HL	-2.01	-1.98	-1.91	-0.82	-0.73	-0.64
ARAGONITE	HH	1.68	1.42	1.84	1.82	1.57	1.69
	LL	1.27	1.21	2.15	1.59	1.55	1.68
	LH	1.58	1.23	1.34	2.14	1.38	1.89
	HL	2.07	1.38	1.50	1.69	1.44	1.55
CALCITE	HH	1.83	1.56	1.98	1.96	1.72	1.83
	LL	1.41	1.35	2.29	1.73	1.69	1.82
	LH	1.73	1.37	1.48	2.28	1.52	2.03
	HL	2.21	1.52	1.64	1.83	1.58	1.69
DOLOMITE	HH	2.92	2.30	3.11	3.35	2.86	3.01
	LL	2.05	1.86	3.71	2.28	2.80	3.01
	LH	2.61	1.86	2.05	3.94	2.46	3.44
	HL	3.68	2.22	2.41	3.07	2.58	2.75
GYPSUM	HH	-1.68	-1.84	-1.64	-0.57	-0.48	-0.41
	LL	-1.79	-1.90	-1.70	-0.69	-0.49	-0.44
	LH	-1.86	-1.94	-1.72	-0.72	-0.60	-0.46
	HL	-1.82	-1.78	-1.71	-0.63	-0.53	-0.44
QUARTZ	HH	-0.17	-0.17	-1.11	-1.34	-0.65	-0.85
	LL	-0.20	-0.30	-1.12	-1.46	-0.67	-0.86
	LH	-0.15	-0.27	-1.05	-1.15	-0.56	-0.71
	HL	-0.22	-0.31	-1.07	-1.47	-0.77	-0.87

Source: http://www.ndsu.nodak.edu/webphreeq/webphreeq-input.cgi 20090427

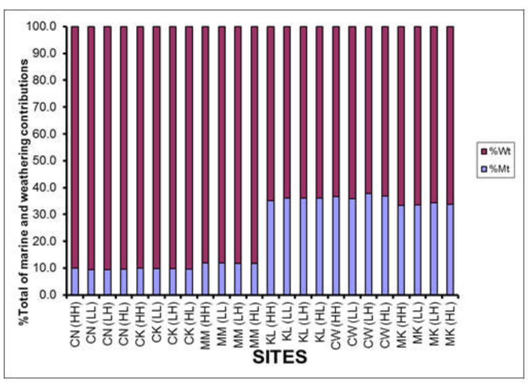

Figure 3: Percentage of marinogenic and weathering contribution to the cave water from different sites at different tides

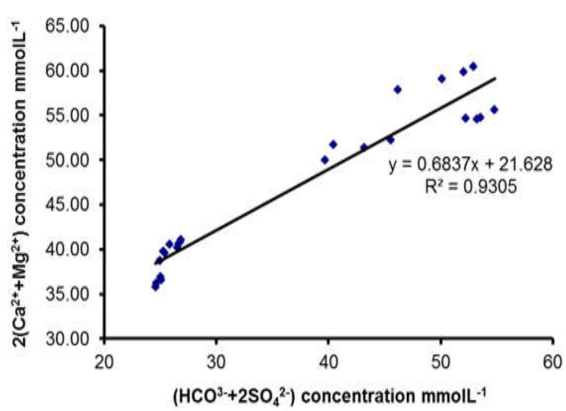

Figure 4: Relationship between summation of bicarbonate and sulphate with summation of calcium and magnesium concentration

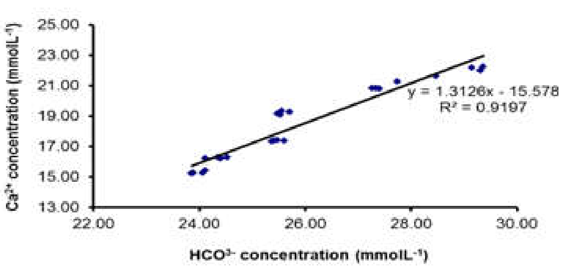

Figure 4: Relationship between Bicarbonate and Calcium concentration

Conclusion

The study of chemical composition of cave water in Zanzibar Island shows that the quality of the water from Chomvi ndogo, Chomvi kubwa, Miza wa Miza, Kilindi, Makutani, and Choweni is affected by tidal change. In this regard the caves have fluctuated concentrations of major elements with reference to sea tides. This is due to several factors such as mineral dissolution, agricultural activities, as well as sea water intrusion. Two major sources, marinogenic and non marinogenic (weathering) can explain the chemical species in ground water. The trend for concentration contributed from marine water was similar to all sampling sites which was K<Ca<Mg<SO_4<Na. Therefore marinogenic, sodium showed a higher percentage concentration. The trend for weathering contribution was SO_4< K Mg<Na<Ca at Chomvi ndogo, Chomvi kubwa and Miza wa Miza caves while Kilindi, Choweni and Makutani the trend was Mg<K <SO_4 <Na <Ca. These trends show that Na contribute more in marinogenic content in all caves while weathering is contributed more by Calcium (Ca) in all sampling sites. But the percentage of marinogenic an weathering contribution to the caves make it different. Marinogenic and weathering percentages were less than 13% and greater than 87% respectively at Chomvi ndogo, Chomvi kubwa and Miza wa Miza but at Kilindi, Choweni and Makutani it were greater than 33% and less than 77% respectively. Summation of magnesium and calcium also shows significant correlation with bicarbonate plus sulphate indicating the dissolution of calcite, dolomite, anhydrite, gypsum and aragonite. The saturation indices from the water cave as calculated by PHREEQC program shows that the dissolution of calcite and aragonite minerals contribute more to concentration of Ca^{2+} and HCO_3^- compared to dolomite, anhydrite and gypsum.

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