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ORIGINAL PAPER

Evaluation of the mineralizing potential of the Mbengwi plutonics, Northwestern Cameroon, Central Africa

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Abstract

The Mbengwi area consists of Cenozoic alkaline rocks and Pan-African calc-alkaline plutonics. The alkaline magmatic series include volcanics (basanites, hawaiites, mugearite, and rhyolite) and syenites while the calc-alkaline plutonics comprise various granitoids (granites, granodiorites, quartz monzonites, and monzonites) associated with monzodiorites. These plutonics are calc-alkaline, metaluminous to weakly peraluminous, mostly I-type, displaying high potassic to shoshonitic affinities. Their magmas are relatively evolved and typically result from melting of the lower continental crust with variable involvement of the oceanic crust. According to the ranges of their Rb/Sr, Zr/Hf, and K/Rb ratios, these magmas have mostly not undergone post-magmatic hydrothermal activity which would lead to mineralization. With regard to their contents in certain elements such as Sr, Rb, and Ba in addition to their gradient in Sm/Eu and Rb/Ba ratios, the Mbengwi plutonics are typical of granitoids devoid of U and Ta deposits. They are also barren in Sn, W, and Mo but mostly productive regarding Cu, Zn, and Fe (Au) skarn.

Keywords Cameroon · Central Africa · Pan-African · Calc-alkaline plutonics · Mineralizing potential

Introduction

Determining the mineralizing potential of intrusive bodies is important because every specific type of granite is usually accompanied with a specific type of ore deposit. Numerous precious metal deposits are spatially, temporally, and genetically associated to various types of granitic rocks (Eugster 1985; Sillitoe 1996). It had been proved that most Sn, W and several rare metal (Ta, Nb, Li, Be, Zr, Ga, REE) deposits, above 60% of Cu resources, approximately 10% of Fe, Au, Zn, Pb, Ag and U, in addition to many minor metals (Bi, Cd, Sb, Te, Re, In, Sc) are related to granitic rocks (Sillitoe 1996). Furthermore, Ghodsi et al. (2016) found that, calc-alkaline I-type magmas have a high ability to bear and concentrate base metals, notably Fe, Cu, Mo, and Au, while S-type magmas involve aqueous fluids containing Sn, W, and base metals.

Although it has been evidenced that Neoproterozoic granitoids from Cameroon host various deposits such as rare metals (Sn-W-REE; Milesi et al. 2006), very few particular attention has been focused on the geology and mineral potential of western Cameroon. Moreover, the studied area has never been so far subject of any mining exploration study. However, Mbassa (2015) revealed unusual remarkable high contents of the Mbengwi plutonics in certain elements such as Cu, Sn, Th, Pb, and Zn, which deserve a particular attention. In this paper, field works, petrographic features, and geochemical analysis are compiled to differentiate the Mbengwi Pan-African rocks either as productive or barren. We are looking forward to clarify if there may be a relationship between the geochemical composition of the studied plutonics and a possible metal mineralization. Therefore, this paper targets to

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evaluate the mineralizing potential of the Mbengwi plutonic rocks, in comparison with the worldwide renowned productive or sterile magmatic rocks.

Geological setting

The Central African fold belt (CAFB; Fig. 1) known as a witness of the Pan-African orogeny in Cameroon is represented by granitic rocks and meta-volcano–sedimentary formations. This CAFB is divided into three domains: (i) the southern nappes consisting of Pan-African metamorphic units which was thrust onto the Archean Congo craton towards the south; (ii) the central area or Adamawa–Yadé domain, bounded by the Sanaga and Tcholliré–Banyo faults (Fig. 1b), consists of Neoproterozoic metasedimentary series and various syn- to post-kinematic calc-alkaline granitoids; (iii) the northern domain that consists of the Neoproterozoic volcano–sedimentary schists, gneisses, and orthogneisses. Overall, the granitic rocks cover a significant surface both in central and western Cameroon. They derived from different sources such as lithospheric mantle (Tchameni et al. 2006; Djouka-Fonkwé et al. 2008), lower continental crust (Nzolang et al. 2003; Nzenti et al. 2006; Mbassa et al. 2016), or mixing between those two components (Njanko et al. 2006; Kwékam et al. 2010, 2013).

The studied zone is circumscribed between the parallels 6°06′ and 5°58′ North and the meridians 9°57′ and 10°06′ East, and lithologically marked by the presence of Pan-African plutonics, Cenozoic magmatic rocks, and sedimentary series (Fig. 1c). The Cenozoic bimodal alkaline magmatic series consist of lavas and syenites belonging to the same magmatic episode (Mbassa et al. 2012). The composition of volcanic rocks ranges from basanite to rhyolite, with a gap between 50 and 62 wt.% SiO_2. Mafic lavas display OIB features and HIMU mantle isotopic signature (Mbassa et al. 2012). The Pan-African plutonics consist of monzodiorites and a continuous granitic series extending from monzonites to granites. They mostly belong to an I-type suite displaying high-potassic calc-alkaline to shoshonitic features (Mbassa et al. 2016). Actually, apart from some alluvial surveys carried out by Dumort (1968) and Peronne (1969) indicating indices of gold, rutile, iron, and manganese, no intensive prospection activity has yet been carried on the studied area.

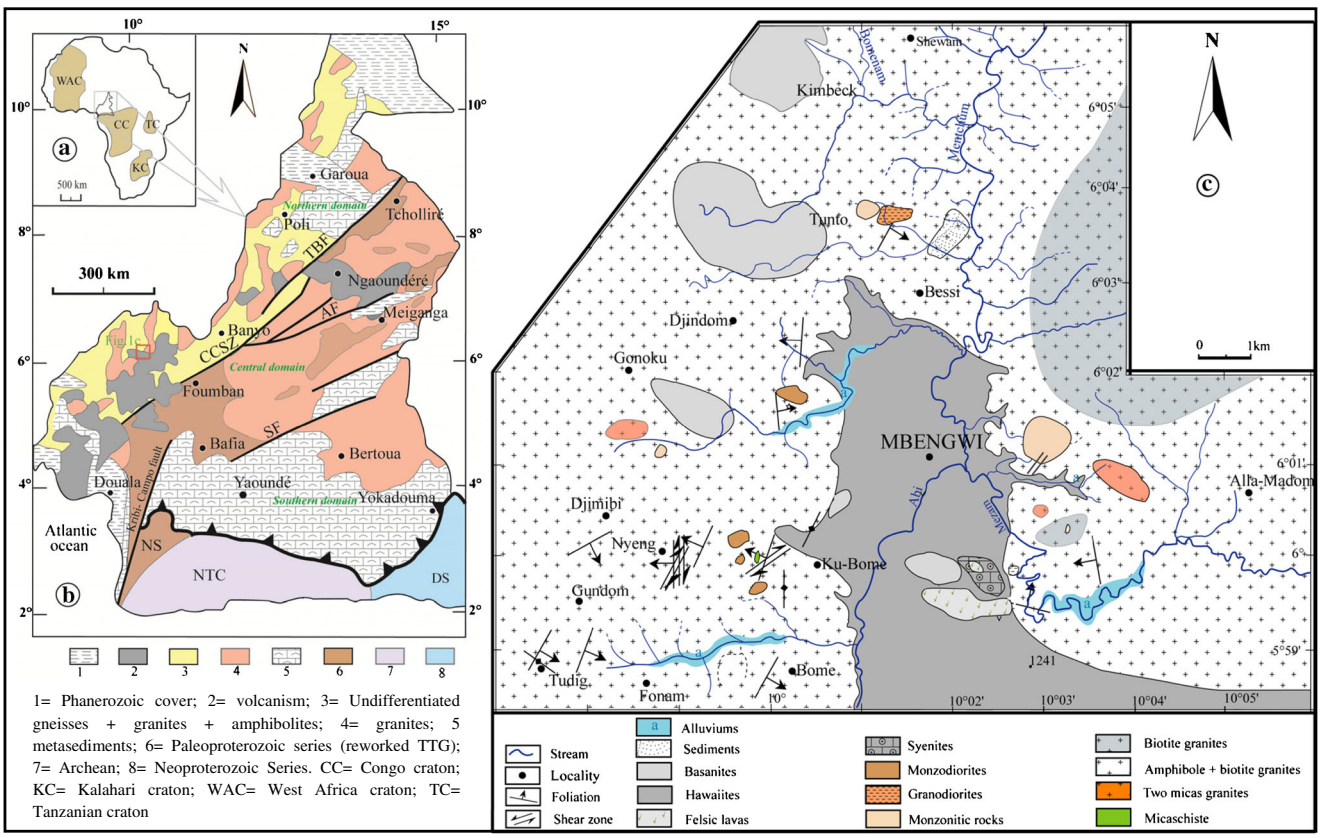

Fig. 1 Geological setting of the studied area. **a** Location of Cameroon in Africa. **b** Simplified geological map of Cameroon showing the main Pan-African domains. AF Adamawa fault, SF: Sanaga fault, TBF: Tcholliré–Banyo fault, CCSZ: central Cameroon shear zone, NTC:Ntem complex, DS: Dja series, NS: Nyong series. **c** Geologic sketch map of the studied area

Analytical methods

A set of 32 representative samples of Pan-African rocks from Mbengwi including granites, granodiorites, monzonites, quartz-monzonites, and monzodiorites were chosen for this study. Major elements were analyzed by ICP-OES and trace elements by ICP-MS, respectively, at the laboratories of *École des mines de Saint-Etienne* (France) and *Geosciences Environnement Toulouse* (GET-OMP, University of Toulouse 3, France). International geostandards were used. Weis and Frey (1991), Benoit et al. (1996), and Aries et al. (2000) describe analytical methods in details. The detection limits for trace elements range between 10^{-2} ppm (REE) and 20 ppm (Zr).

Mineral major element compositions were determined with a CAMECA SX 50, at the service of microanalysis and microscopy of *Geosciences Environnement Toulouse* (GET-OMP, University of Toulouse 3, France). Analytical conditions were 15 kV for the acceleration tension, and the beam size was 2 × 2 μm under 10 or 20 ηA, according to resistance of mineral to the electronic beam. Acquisition times were 10 s for the peak and 5 s on both sides of the peak, for an analyzed volume of 5 μm^3; Kα lines were used.

Petrography and geochemistry

Plutonics from Mbengwi consist of coarse-grained granitic rocks and fine-grained monzodiorites. Granitic rocks include monzonites, quartz-monzonites, granodiorites, and granites (biotite granites, amphibole-biotite granites, and two-mica granites). The monzodiorites ($An_{27.2–44.1}$) outcrop within granitoids as small subrounded or elongated enclaves. The leading mineral phase assemblage including quartz (Qtz), K-feldspar, plagioclase, amphibole, and biotite is completed by muscovite in two-mica granites. The accessory phase includes ilmenite, magnetite, sphene, apatite, and zircon. Biotite (Bt) is locally transformed to chlorite or prehnite, amphibole to chlorite, epidote or calcite, and ilmenite to goethite.

Whole rock geochemical analysis for representative plutonic samples from Mbengwi including major and trace elements are listed in Table 1. The studied calc-alkaline plutonics are mainly volcanic-related, metaluminous to weakly peraluminous (Fig. 2a) and their SiO_2 contents range between 48 and 77.9 wt.%. Only one sample (E_{125}: A/NK = 0.98) can be considered as peralkaline although it contains Mg-biotites. They are of I-type with high-K to shoshonitic affinities. However, one sample of two-mica granites has typical S-type features, suggesting either the sedimentary nature of the protolith or the assimilation of sedimentary xenoliths (Mbassa et al. 2016). The studied plutonics are strongly fractionated ($(La/Lu)_N$ = 4.05–102.96) and characterized by LILE and LREE enrichment compared with HFSE and HREE respectively. They also display negative Rb, K, Sr, P, Ti, Eu, and positive Th and La anomalies (Fig. 2b, c); such features are consistent with a subduction environment.

The Sr and Nd isotopic compositions of these plutonics evidence the involvement of heterogeneous crustal materials including both the lower continental and oceanic crusts during the melting processes. The Mbengwi plutonics are then specific; since the other Pan-African high-K calc-alkaline plutons from western and central Cameroon are all melting products of the continental crust only (Mbassa et al. 2016).

Discussion

As it has been mentioned above, Mbengwi plutonics are predominantly of I-type and coexist with small outcrops of S-type rocks. According to Nédélec and Bouchez (2011), such granitoids are known to be enriched respectively in chalcophile (Cu, Ag, Zn, Ga ...) and lithophile (Sn, W, U, Nb, Ta, Be, and Li) elements. Thus, several geochemical indicators have been used to differentiate potential productive granitoids from barren ones. The comparison of the studied plutonics contents in some elements of metallogenic interest such as Cu, Sn, Pb, Th, and Zn with their Clarke as shown in Table 2 reveals that they possess interesting chemical enrichment clues. The results are discussed below.

Sn and W mineralization

The degree and type of differentiation and oxidation state of the magma that formed granites are important to determine the potential and type of associated mineralization (Blevin 2003). The Mbengwi plutonics have SiO_2 (48.11–77.90 wt.%) and K_2O (1.65–7.21 wt.%) contents in the range of Sn- and W-related granitoids, and K/Rb ratios between 132 and 955. They are mainly moderately evolved (Fig. 3a). Highly evolved granitoids, indicators of Sn, W, U, Li, Be, and REE mineralizing potential, have K/Rb ratios under 100 (Rossi et al. 2011), and Sn-related granitic rocks are predominantly of S-type (Govett and Atherden 1988). Consequently, the predominant I-type nature of the Mbengwi granitoids and their high K/Rb ratios (132–955) do not favor high concentration of the above trace and rare earth elements. The Mbengwi plutonics display high Sr, Rb, and Ba contents in addition to Sm/Eu and Rb/Ba ratios compared to related porphyry tin deposits (data from Lehmann and Mahawat 1989; Pei and Hong 1995) (Fig. 3b), meaning that the studied plutonics might not be fertile regarding tin mineralization. Otherwise, Karimpour and Bowes (1983) used diagrams such as Rb/Sr and Ce/Yb ratios versus color index ($[CI = (SiO_2 + K_2O + Na_2O)/(MgO + CaO + FeO)]$) to differentiate granitoids and identify their economic potential for tin, molybdenum, or copper (Fig. 4a, b). The Mbengwi granitoids when plotted in those

Table 1 Representative whole rock major oxides (wt.%), trace elements (ppm), and rare earth elements (ppm) for plutonic samples from the Mbengwi

	Monzodiorites						Monzonites		Qtz-monzonites						Granodiorites	
	E141	E134	E131	E135	E142	E33	E63	E69b	E144	E42	E67	E64	E65	E125	E41	E54
SiO_2	48.81	48.11	51.44	54.84	55.58	50.37	61.92	60.81	66.90	63.24	62.11	67.57	68.07	69.80	66.64	64.93
TiO_2	1.47	1.82	1.41	1.28	1.15	1.62	1.48	0.96	0.99	1.05	1.47	0.50	0.46	0.34	0.67	0.64
Al_2O_3	15.37	17.11	16.74	16.96	16.33	19.43	16.15	14.35	15.79	15.66	16.10	15.98	16.13	14.26	15.69	17.05
Fe_2O_3	1.38	1.50	1.28	1.02	1.09	1.28	0.79	0.88	0.58	0.89	0.79	0.64	0.72	0.51	0.96	0.58
FeO	9.19	10.00	8.54	6.79	7.24	8.51	5.26	5.88	2.57	5.92	5.26	2.84	2.40	1.71	4.27	3.85
MnO	0.17	0.16	0.20	0.12	0.23	0.12	0.08	0.14	0.05	0.11	0.08	0.04	0.05	0.04	0.09	0.11
MgO	8.39	6.51	6.19	3.91	5.28	3.94	1.91	2.85	1.19	1.17	1.79	0.64	0.47	0.75	1.59	1.70
CaO	9.47	8.81	8.22	6.77	6.07	7.04	4.25	5.34	2.57	3.16	4.06	1.70	1.37	1.95	3.28	3.93
Na_2O	3.00	3.12	3.32	3.88	4.08	4.77	3.61	3.03	3.74	4.07	3.74	3.53	4.26	5.52	4.88	4.61
K_2O	2.22	2.65	2.34	3.75	2.55	2.39	4.12	5.59	5.28	4.44	4.18	6.40	5.96	5.01	1.65	2.35
P_2O_5	0.53	0.21	0.31	0.68	0.40	0.53	0.42	0.17	0.35	0.30	0.43	0.15	0.11	0.11	0.28	0.25
Total	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100
Ag	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
Ba	849	660	322	2010	300	1185	1540	473	1560	1585	1720	999	937	764	259	855
Co	47.3	46	42.6	42.5	38.5	35	30.2	28	47	38.1	48.5	39.9	30.9	44.3	31.2	38.8
Cr	370	30	70	10	200	< 10	10	30	< 10	< 10	10	< 10	< 10	< 10	10	< 10
Cs	4.54	4.76	7.14	1.48	8.25	3.56	9.55	1.17	8.12	11.55	2.82	6.02	10.15	4.17	4.53	2.14
Cu	39	68	37	238	114	23	6	22	15	12	13	< 5	< 5	< 5	29	< 5
Ga	21.7	21.9	24.4	22	31.9	26.5	24.7	23	26	24.9	25.5	25.2	25.3	19.6	26.4	25.5
Hf	2.6	3.1	2.2	6.4	13.6	8.3	9.9	8.1	8.6	11.3	10.6	12.3	15.3	6.7	6.1	7.1
Mo	< 2	< 2	2	< 2	< 2	< 2	< 2	< 2	< 2	2	< 2	< 2	2	< 2	< 2	< 2
Nb	11.3	9.9	15.3	17.2	27.2	13.1	25.5	29.8	29.5	31.2	25.5	26.1	15.7	13.3	11.2	15.8
Ni	93	28	35	13	67	15	8	19	5	< 5	6	< 5	< 5	< 5	< 5	< 5
Pb	14	11	13	25	16	13	23	25	32	29	24	29	28	27	18	25
Rb	120	126	154	104.5	180.5	114	182.5	113	238	178	170.5	156.5	199	178.5	91.1	80
Sn	3	3	6	3	10	2	3	2	6	4	3	2	1	2	5	6
Sr	862	564	490	882	346	1040	555	195.5	683	390	600	233	166.5	272	262	540
Ta	0.6	0.7	1.1	1.4	1	0.7	1.4	2	2.9	2.1	1.4	1.1	0.3	1.3	0.8	1.4
Th	3.67	3.48	5.72	12.85	14.55	3.67	14.3	17.25	26.2	12.7	16.05	26.6	28.9	44.4	8.99	36.3
Tl	0.5	0.5	0.6	< 0.5	0.6	0.5	0.8	0.5	1	0.7	0.7	0.7	0.9	0.7	< 0.5	< 0.5
U	0.66	1.61	1.77	4.14	4.64	0.9	3.68	3.12	7.96	4.08	2.41	2.77	4.39	2.34	1.8	5.02
V	246	349	246	189	138	204	72	96	57	44	72	18	9	33	76	66
W	22	25	39	56	61	29	78	55	206	143	179	188	151	224	114	154
Zn	123	122	155	89	216	142	124	152	76	124	128	86	88	43	104	113

Table 1 (continued)

Zr	69	105	64	238	497	327	404	282	295	466	430	466	580	213	218	259
Y	23.1	19.5	32.8	31.4	65.4	20.2	16.5	36.2	34	31.6	17.2	30.5	28.4	17.2	21.9	32.1
La	34.8	19.4	28.1	46.9	38.7	41.9	149.5	72.7	82.4	74.1	100	166	130	45.2	29.9	62.7
Ce	70.6	42	57.6	105	93.4	92.6	227	135	183.5	141.5	177	294	285	85.5	61.3	119.5
Pr	8.16	5.11	8.1	12.05	14.1	11.6	22.3	15.85	20.3	15.85	18.45	29.6	25.3	8.49	7.11	12.65
Nd	33.8	22.7	36.8	48.1	66.3	49.1	73.3	60.9	75.7	61	65.6	102	87.3	29.6	30.2	46.5
Sm	6.87	5.09	8.56	8.86	16.7	9.3	9.68	10.85	12.2	10.5	9.64	15	13.5	5	7.02	8.67
Eu	2.04	1.56	1.9	2.79	2.36	2.65	2.4	1.01	2.3	2.43	2.27	1.42	1.41	0.97	1.37	1.52
Gd	6.46	4.88	7.76	7.93	14.4	7.71	8.51	9.88	9.74	9.13	7.74	13.15	12.15	4.56	6.34	7.86
Tb	0.95	0.75	1.21	1.18	2.28	1.04	0.91	1.45	1.14	1.29	0.91	1.63	1.52	0.63	0.9	1.18
Dy	4.73	3.95	6.49	6	12	4.7	3.64	7.29	5.02	6.27	3.76	7.16	6.8	3.24	4.38	6.24
Ho	0.9	0.75	1.23	1.16	2.31	0.75	0.63	1.4	0.97	1.17	0.65	1.27	1.19	0.62	0.82	1.19
Er	2.49	2.13	3.5	3.37	6.56	1.92	1.77	3.96	2.89	3.43	1.8	3.4	3.25	1.83	2.27	3.53
Tm	0.31	0.29	0.49	0.48	0.94	0.22	0.2	0.55	0.37	0.45	0.21	0.39	0.37	0.27	0.32	0.5
Yb	1.89	1.78	3.13	3.04	5.87	1.26	1.23	3.45	2.42	2.93	1.26	2.34	2.22	1.79	1.97	3.08
Lu	0.29	0.26	0.46	0.5	0.9	0.18	0.18	0.53	0.42	0.45	0.18	0.34	0.33	0.27	0.3	0.44
A/NK	2.95	2.97	2.95	2.22	2.46	2.72	2.09	1.67	1.75	1.84	2.03	1.61	1.58	1.35	2.40	2.45
A/CNK	1.05	1.17	1.21	1.18	1.29	1.37	1.35	1.03	1.36	1.34	1.34	1.37	1.39	1.14	1.60	1.57
Sm/Eu	3.37	3.26	4.51	3.18	7.08	3.51	4.03	10.74	5.30	4.32	4.25	10.56	9.57	5.15	5.12	5.70
Rb/Sr	0.14	0.22	0.31	0.12	0.52	0.11	0.33	0.58	0.35	0.46	0.28	0.67	1.20	0.66	0.35	0.15
Zr/Hf	26.54	33.87	29.09	37.19	36.54	39.40	40.81	34.81	34.30	41.24	40.57	37.89	37.91	31.79	35.74	36.48
Sr/Y	37.32	28.92	14.94	28.09	5.29	51.49	33.64	5.40	20.09	12.34	34.88	7.64	5.86	15.81	11.96	16.82
	Amph+ Bt-granite			Bt-granites								Two-mica granite				Leucocratic granite
	E68	E69	E611	R2	E2	E6	E12	E20	E53	E126	E129	E145	E610	E60	E62	E66
SiO_2	71.42	71.57	72.46	72.67	71.81	70.83	75.36	77.51	77.24	72.93	71.60	72.36	74.06	69.65	74.32	77.90
TiO_2	0.35	0.38	0.38	0.26	0.33	0.46	0.36	0.09	0.15	0.28	0.23	0.48	0.18	0.43	0.08	0.03
Al_2O_3	13.74	13.77	14.48	14.25	14.24	14.78	12.13	12.95	12.50	14.08	14.72	13.84	14.36	15.45	14.46	12.36
Fe_2O_3	0.81	0.79	0.46	0.35	0.50	0.42	0.50	0.13	0.15	0.42	0.48	0.59	0.46	0.50	0.19	0.05
FeO	2.69	2.62	1.54	1.17	1.67	1.41	1.65	0.45	0.49	1.39	1.60	1.96	1.53	2.24	0.62	0.17
MnO	0.06	0.07	0.07	0.04	0.05	0.03	0.04	0.01	0.01	0.03	0.03	0.03	0.06	0.04	0.03	0.00
MgO	0.26	0.23	0.13	0.39	0.66	0.56	0.22	0.16	0.17	0.50	0.56	0.88	0.27	0.69	0.20	0.06
CaO	1.00	0.85	0.97	1.24	1.35	1.47	0.39	1.63	0.78	1.42	1.29	2.04	0.54	1.65	0.98	0.39
Na_2O	3.93	3.70	3.36	3.58	3.10	4.32	2.21	3.98	3.02	3.09	3.20	3.38	3.13	3.62	4.16	2.71
K_2O	5.68	5.97	6.16	5.95	6.18	5.57	7.12	3.04	5.45	5.78	6.22	4.29	5.41	5.59	4.89	6.30
P_2O_5	0.06	0.05	0.00	0.09	0.11	0.14	0.02	0.02	0.02	0.08	0.08	0.15	0.00	0.14	0.07	0.02
Total	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100
Ag	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
Ba	319	293	233	1735	903	1220	953	313	1195	1160	1175	1220	203	1275	797	700
Co	52	56.8	36.5	50.5	53.1	51	57.1	62.1	79.3	55.2	47.7	57.8	46.7	44.7	55	81.2
Cr	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	10	< 10	< 10	< 10	< 10
Cs	1.7	1.53	0.58	2.54	4.52	3.44	4.04	2.54	1.81	4.06	3.31	9.07	10.2	3.02	5.46	3.42
Cu	< 5	6	< 5	< 5	10	< 5	< 5	< 5	5	< 5	5	< 5	< 5	< 5	< 5	5
Ga	25.4	24.1	23.1	19.3	19.4	21.2	17.3	17.5	14.6	19.9	20.1	23	26.6	23.6	22.2	22.5
Hf	15.5	16.5	18.3	5.8	5.7	8.2	12.1	2.7	2.7	5.7	11.6	6.5	2.7	7.7	2.4	11.3
Mo	< 2	< 2	2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2

Table 1 (continued)

Nb	28.3	30.3	27.4	11.2	7.6	13.6	17.1	4	5.4	10	6.5	13.3	33.7	10.6	12.7	3.3
Ni	< 5	< 5	< 5	< 5	5	< 5	< 5	8	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5
Pb	26	25	19	30	32	33	40	22	30	32	35	23	39	33	42	47
Rb	119.5	113.5	64.5	170.5	206	155.5	219	86.8	142	194.5	187.5	188.5	230	151	170	170.5
Sn	2	1	1	1	2	3	4	1	2	2	1	3	10	3	4	< 1
Sr	78.9	71.2	62.7	482	314	341	178.5	217	368	366	389	706	73.3	312	177	398
Ta	1.4	1.5	1.1	1	0.6	0.9	2	0.8	0.6	1.3	0.7	1.4	3.5	0.6	1.3	0.2
Th	37.6	34.4	41.5	30.1	16.55	18.4	23.7	8.19	34.5	44.8	126	30	13.4	17.1	8.59	24
Tl	0.5	0.5	< 0.5	0.6	0.8	0.7	0.9	< 0.5	0.6	0.9	0.8	0.7	1	0.7	0.9	0.6
U	2.73	2.22	1.31	5.08	1.34	2.02	2.83	1.19	3.05	2.23	5.75	6.05	2.6	1.86	3.96	2.59
V	8	6	< 5	19	23	9	11	5	13	23	36	40	< 5	18	< 5	< 5
W	269	292	190	259	256	252	297	328	419	278	234	285	246	217	294	433
Zn	95	88	71	30	64	43	42	16	15	42	36	70	102	63	43	< 5
Zr	648	681	809	194	191	303	408	73	83	186	350	219	59	291	59	250
Y	31.6	28.3	18.6	10.9	51.5	10.8	103	9.5	9.8	15.3	9.2	11.4	19.2	16.1	14.7	3.4
La	284	242	367	79.1	75	110	55.6	20.6	122	100.5	110.5	77.8	29.3	114	19.9	9.7
Ce	406	402	661	147.5	101	177.5	96.2	18.3	189.5	156.5	258	126	54.2	183	37.7	13.3
Pr	50.4	43	66.4	14.55	12.1	16.35	14.4	2.73	16.45	17.3	22.4	11.5	6.37	18.75	4.16	1.12
Nd	176.5	151.5	232	50	42.2	51.8	65.2	9.5	50.8	57.7	73.4	37.9	24.1	63.6	15.5	3.6
Sm	21.1	18.95	25.4	7.1	5.98	6.24	17.8	1.52	5.91	7.91	9.74	5.55	5.43	8.76	3.38	0.76
Eu	0.78	0.63	0.61	1.37	1.13	1.08	2.68	0.64	0.88	1.18	1.17	1.16	0.38	1.32	0.68	0.11
Gd	16.9	16	19.7	5.52	6.26	5.18	21.8	1.64	5.2	6.48	7.26	4.78	5.02	7.75	3.22	0.7
Tb	1.76	1.67	1.73	0.57	0.82	0.54	4	0.24	0.52	0.74	0.67	0.55	0.75	0.85	0.49	0.12
Dy	6.78	6.75	5.41	2.32	4.65	2.16	23.4	1.17	2	3.12	2.27	2.36	3.85	3.48	2.59	0.68
Ho	1.22	1.15	0.87	0.43	1.15	0.39	4.55	0.25	0.36	0.57	0.38	0.42	0.69	0.59	0.48	0.15
Er	3.67	3.47	2.72	1.26	3.79	1.21	11.65	0.79	1.07	1.71	1.18	1.19	1.86	1.63	1.37	0.46
Tm	0.46	0.42	0.28	0.17	0.5	0.15	1.43	0.12	0.14	0.23	0.14	0.15	0.25	0.17	0.16	0.09
Yb	2.92	2.75	2.05	1.07	2.78	1.06	7.64	0.89	0.93	1.48	1.04	1.08	1.53	1.09	1.02	0.5
Lu	0.51	0.45	0.37	0.17	0.49	0.17	0.92	0.15	0.13	0.21	0.17	0.15	0.23	0.17	0.15	0.09
A/NK	1.43	1.42	1.52	1.49	1.54	1.50	1.30	1.84	1.48	1.59	1.56	1.81	1.68	1.68	1.60	1.37
A/CNK	1.30	1.31	1.38	1.32	1.34	1.30	1.25	1.50	1.35	1.37	1.38	1.43	1.58	1.42	1.44	1.31
Sm/Eu	27.05	30.08	41.64	5.18	5.29	5.78	6.64	2.38	6.72	6.70	8.32	4.78	14.29	6.64	4.97	6.91
Rb/Sr	1.51	1.59	1.03	0.35	0.66	0.46	1.23	0.40	0.39	0.53	0.48	0.27	3.14	0.48	0.96	0.43
Zr/Hf	41.81	41.27	44.21	33.45	33.51	36.95	33.72	27.04	30.74	32.63	30.17	33.69	21.85	37.79	24.58	22.12
Sr/Y	2.50	2.52	3.37	44.22	6.10	31.57	1.73	22.84	37.55	23.92	42.28	61.93	3.82	19.38	12.04	117.06

diagrams indicate that they remain unproductive in Sn and Mo, and rather fertile regarding Cu. Elsewhere, special minerals such as tourmaline and topaz are known to be symptomatic of tin (Sn) mineralization (Rozendaal and Bruwer 1995); therefore, the non-appearance of tourmaline and topaz in the studied rocks evidences that the mineralization of tin is unlikely. The high Sn content of some granites may be justified by the fact that as Sn is hosted by muscovite, its content will increase proportionally with the amount of muscovite during differentiation process (Neiva et al. 2002). Generally, granitic rocks hosting Sn, U, and W mineralization commonly have high phosphorus concentration (Ruiz et al. 2008). Furthermore, Bea et al. (1992) specified that P_2O_5 contents greater than 0.5 wt.% in rocks having more than 70 wt.% SiO_2 are good indicators of economic mineralization. Taking into consideration this last statement, we realize that in Mbengwi, only granites have SiO_2 contents greater than 70 wt.% and their average P_2O_5 content is somewhat less than 0.5 wt.%.

Zn mineralization

Wolfe (1977) and Lentz (1998) established a relation between the SiO_2 content and the amount of Zn in granitoids. Zn amount is fixed (≈ 85 ppm) for intermediate rocks, decreases linearly with increasing SiO_2 in rocks having more than 60 wt.% SiO_2 and reaches 35 ppm in rocks with 75 wt.% SiO_2. Almost all the studied rocks except the leucocratic granite (E_{66}) contain Zn with amount ranging from 15 to 216 ppm. On the other hand, Wolfe (1977) stated that all rocks containing more than 10 wt.% of total iron may be good targets in regional explorations of zinc, and therefore suggested the use of SiO_2 vs. Fe and SiO_2 vs. Zn discriminating diagrams to decipher the sterile or fertile nature of plutonics regarding Zn detection. These diagrams disclose that the Mbengwi granitic rock samples are mostly fertile with regard to zinc (Fig. 5a, b). In mineralogy, despite the non-occurrence in the studied area of Zn-bearing mineral such as sphalerite known as major ore for Zn, the fertile character of the Mbengwi

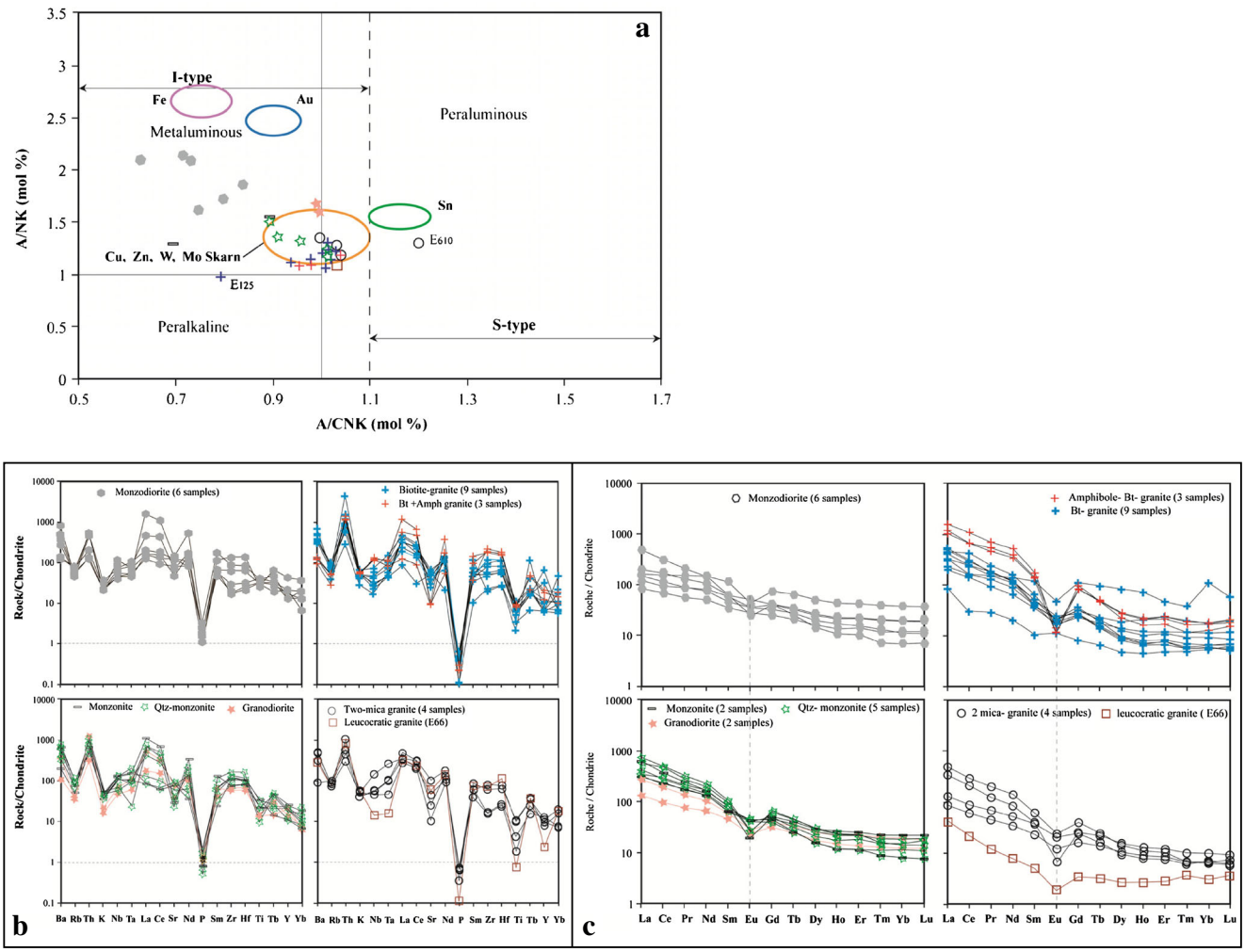

Fig. 2 **a** A/NK vs. A/CNK variation diagram of Maniar and Piccoli (1989) showing the mean composition of the Mbengwi plutonic rocks with related metals. The open circles with respective names are from Meinert (1995). **b** Chondrite-normalized multi-element diagrams. **c** Chondrite normalized rare earth element diagrams for the studied rocks. Normalization value after McDonough and Sun (1995)

Table 2 Comparison of contents of some elements from the Mbengwi plutonics with respect to their Clarke. The Clarke are from Wedepohl (1995)

Element	Amount within the continental crust (ppm)	Amount in the Mbengwi plutonics (ppm)	Enriched rocks	Rate of enrichment
Cu	25	< 5–238 (E_{135})	Monzodiorites (E_{134}, E_{135}, E_{142})	2–9 times
Sn	2	< 1–10 (E_{142}. E_{610})	Monzodiorites (E_{131}, E_{142}). Quartz monzonites (E_{42}, E_{144}). Granodiorites. Bt-granite (E_{12}). Two-mica granites (E_{62}. E_{610})	2–5 times
Pb	15	11–47(E_{66})	Almost all Bt-granites. Two-mica granites and leucocratic granite	2–3 times
Th	9	3.48–126 (E_{129})	Quartz monzonites except E_{42}. Granodiorite (E_{54}). Amph+Bt-granites. Almost all biotite-granites two-mica granite (E_{145})	2–14 times
Zn	65	< 5–216 (E_{142})	Almost all monzodiorite except E_{135}. All monzonites and some quartz monzonites (E_{42}, E_{67})	2–3 times

granitoids regarding Zn is expressed by a significant occurrence of this metal in some biotites, magnetites, chlorites, and calcites. Chlorites and biotites hosting the highest amounts of ZnO (> 0.3 wt.%) are respectively ripidolite and Fe- or Mg-biotites. Those minerals displaying the highest amount of ZnO mostly occur in quartz monzonites (E_{144}, E_{64}), granodiorites (E_{41}, E_{54}), and in a two-mica granite (E_{60}). The estimation of the proximity of unusual Zn concentration and accordingly potential Zn mineralization at surface in semi-arid environments can be made possible using an index based on Zn/Mn ratios in Fe–Mn crusts of Spinks et al. (2017). According to this index, values of Zn/Mn ratios above 0.006 are indicative of the proximity of a probable metal source. Apart from the leucocratic sample (E_{66}) containing no Mn, all the studied samples have Zn/Mn ratios (0.072–0.226) higher than 6×10^{-3}; therefore, samples which are assigned fertile would be mineralized very close to the surface.

Cu mineralization

Copper and zinc behave differently during fractional crystallization process, although their chemical properties are close. Copper is mostly founded in chalcopyrite while zinc substitutes iron in ferromagnesian silicates (Bahajroy and Taki 2014). Usually, copper mineralization are found either above subduction zones in magmatic arcs or in post-collisional settings developed at the end of the subduction (Sillitoe 2010; Richards 2011). In both environments, the discrimination between the productive and the barren rocks regarding copper is routinely based on whole rock geochemistry (Baldwin and Pearce 1982; Asadi et al. 2014; Zarasvandi et al. 2015). The ore-forming granitoids display Sr/Y ratio values higher than 35, low HFSE contents, and absence of pronounced negative Eu anomalies (Shafiei et al. 2009; Hou et al. 2011; Richards et al. 2012;

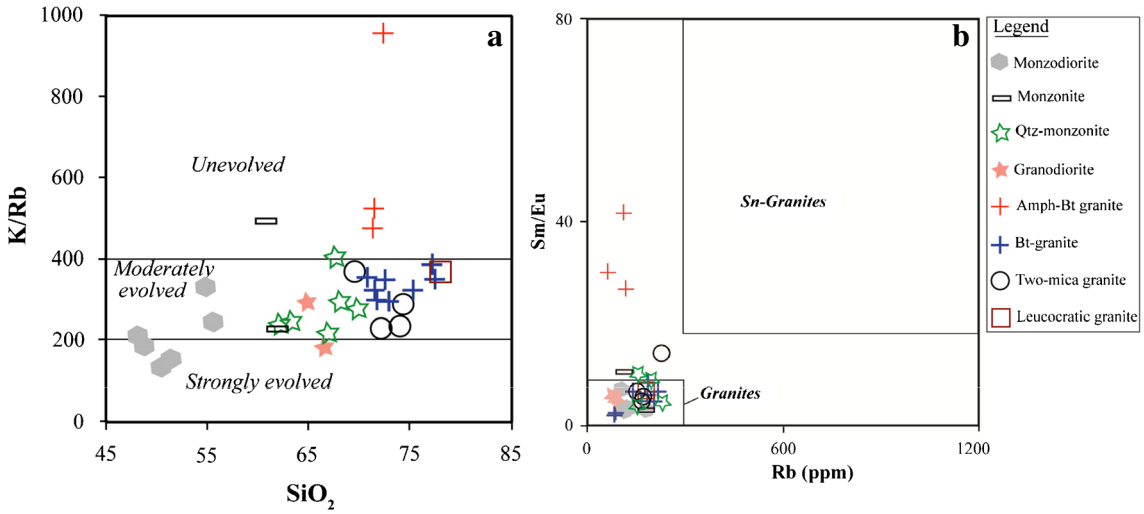

Fig.3 **a** Plot of K/Rb vs. SiO_2 (wt.%) (Blevin 2003). Most studied samples are semi-evolved. **b** Sm/Eu vs. Rb (ppm) diagram discriminating tin-bearing granites from barren ones (Karimpour and Bowes 1983)

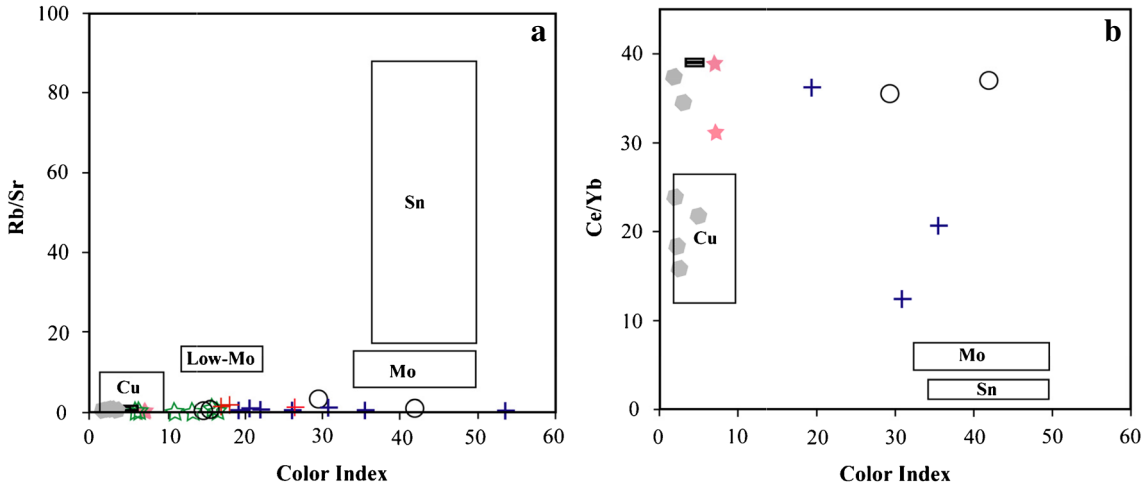

Fig. 4 Discrimination of source rock diagrams of Cu, Sn, and Mo porphyry deposits using a color index and ratios of **a** Rb/Sr and **b** Ce/Yb (Karimpour 1999) and a plot of the study area's samples

Gao et al. 2013; Ahmadian et al. 2015; Wu et al. 2016). The Mbengwi syn- to post-collisional plutonics mainly display lower Sr/Y ratios (with very few samples having Sr/Y > 3, low HFSE contents (Table 1), and overall negative anomaly in Eu).

The use of Sr/Y vs. SiO_2 and Al_2O_3/TiO_2 vs. SiO_2 discriminating diagrams of Loucks (2014) (Fig. 6a, b) reveals that the composition of the Mbengwi plutonics overlaps both barren and productive areas. As shown in Fig. 6a, some granite samples (Bt-granite, two-mica granite, and leucocratic granite) are fertile while other plutonics are unproductive. The majority of samples are relatively barren regarding Cu deposits (Fig. 6b).

The Y versus MnO diagram of Baldwin and Pearce (1982) points out that the Mbengwi plutonics vary from barren to sub-productive and very few fertile granitoids (Fig. 7). Another discriminating diagram (Fig. 2a) also shows a productive nature for the Mbengwi calc-alkaline I-type granitoids regarding Cu and skarn ore deposits.

In order to identify if the magma could release or not hydrothermal phase, Bea et al. (2006) used Zr/Hf ratio as index; when Zr/Hf < 20, magmatic hydrothermal alteration occurred and mineralization processes are favored, and once Zr/Hf > 20, this suggests that there was no hydrothermal alteration. The Mbengwi plutonics Zr/Hf ratio ranges from 21.85 to 44.21, meaning that they have not undergone magmatic hydrothermal alteration. Although some of the previous diagrams evidenced the productive character of the Mbengwi granitoids, their overall negative Eu anomaly (Fig. 2c) is symptomatic of their low potential to be hosting massive Cu deposits.

Skarn mineralization

Generally, skarn mineralizations are often associated either with metaluminous to slightly perluminous rocks or with calc-alkaline granitoids (Meinert 1995) as shown in Figs. 2a

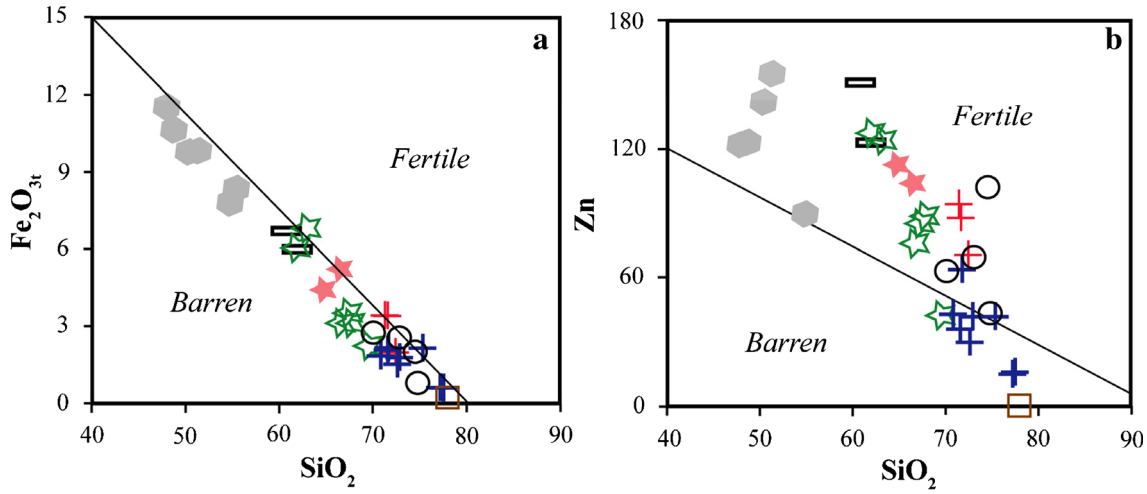

Fig. 5 Representation of the composition of Mbengwi granitoids in **a** Fe_2O_3t (wt.%) and **b** Zn (ppm) vs. SiO_2 (wt.%) of Wolfe (1977) discriminating barren and fertile granites

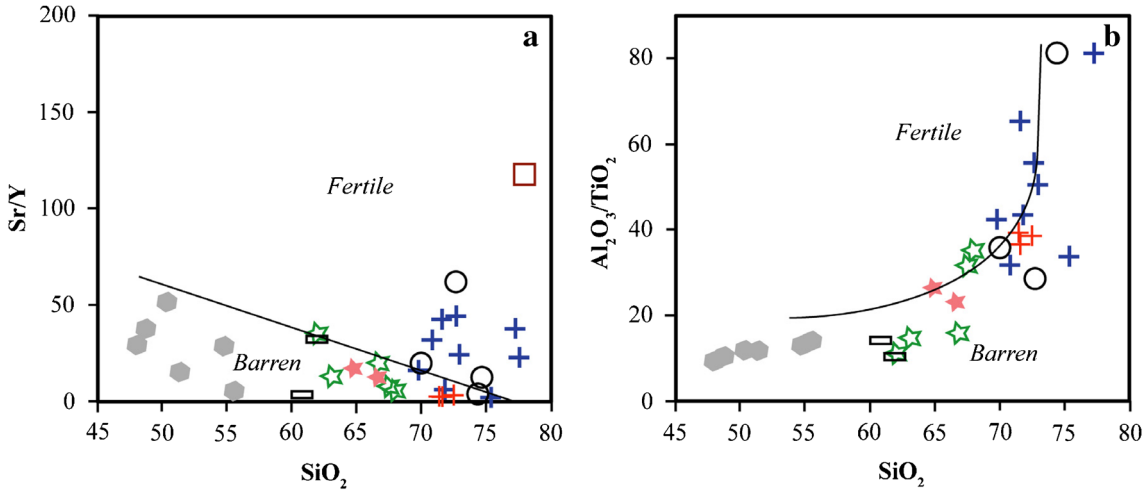

Fig. 6 Plot of whole rock chemistry of the Mbengwi granitoids on discriminating diagrams of Loucks (2014). **a** Sr/Y vs. SiO_2 (wt.%) diagram. **b** Al_2O_3/TiO_2 vs.SiO_2 (wt.%)

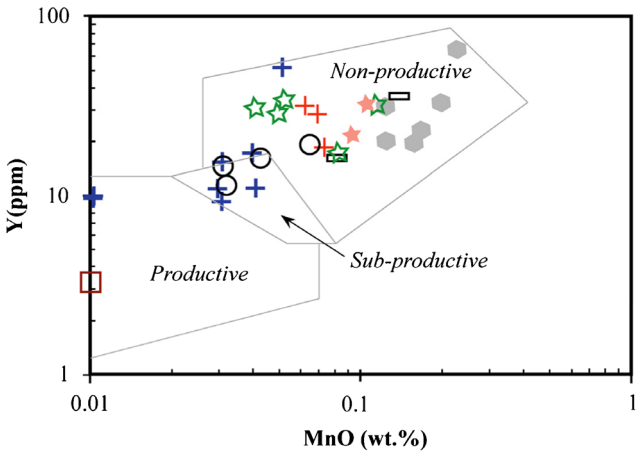

Fig. 7 Whole rock Y vs. MnO diagram of Baldwin and Pearce (1982) for the Mbengwi granitoids

and 8, respectively. The projection of the studied plutonics in the A/CNK vs. A/NK diagram (Fig. 2a) reveals that compositions of some granitoids are essentially comparable to calc-alkaline granitoids associated with Cu, Zn, W, and Mo skarn. Monzodiorites and few intermediate rocks (monzonites, one Qtz-monzonite, and a granodiorite sample) overlap Fe and Cu skarn granitoids fields. In the ($Na_2O + K_2O$) versus SiO_2 diagram, the intermediate phases of the Mbengwi granitic rocks remain close to Zn and Cu skarn-related granitoids (Fig. 8a). Plotting of the studied rocks in the AFM diagram reveals that their compositions seem to be similar to those of granitoids associated with all skarn types (Fig. 8b), although this diagram indicates that compositions of the intermediate phases are alike to magmatic districts related to Zn and Cu mineralization. Using the Nb versus Y and Rb versus (Y + Nb) discriminative diagrams, the compositions of the Mbengwi granitoids

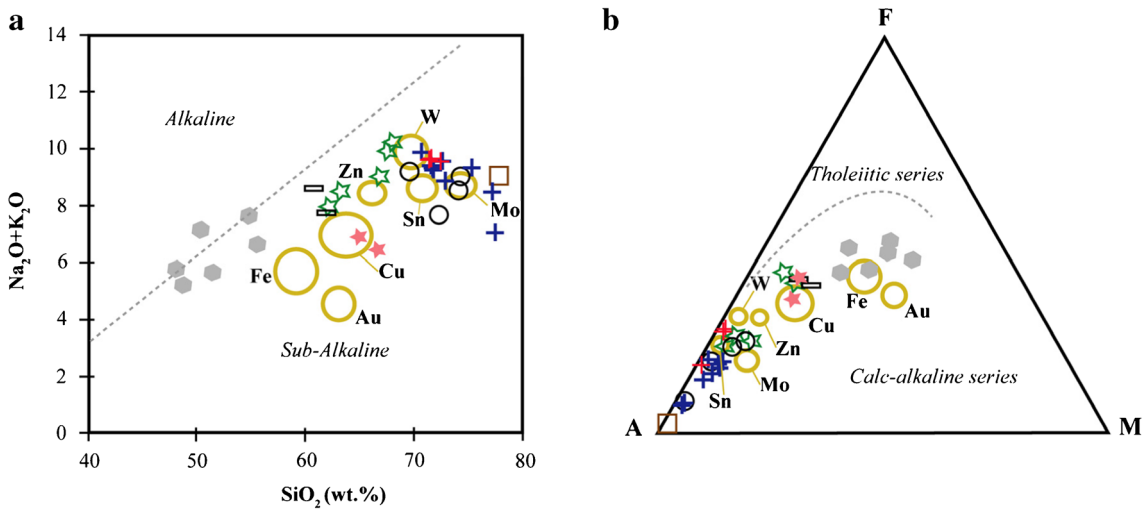

Fig. 8 Plotting of the Mbengwi granitoids composition together with the mean composition of various mineralized granitoids with related metals (of which the names are indicated) are from Meinert (1995) in **a** $K_2O +$ Na_2O (wt.%) vs. SiO_2 (wt.%) of Rickwood (1989) and **b** AFM diagram of Irvine & Baragar (1971)

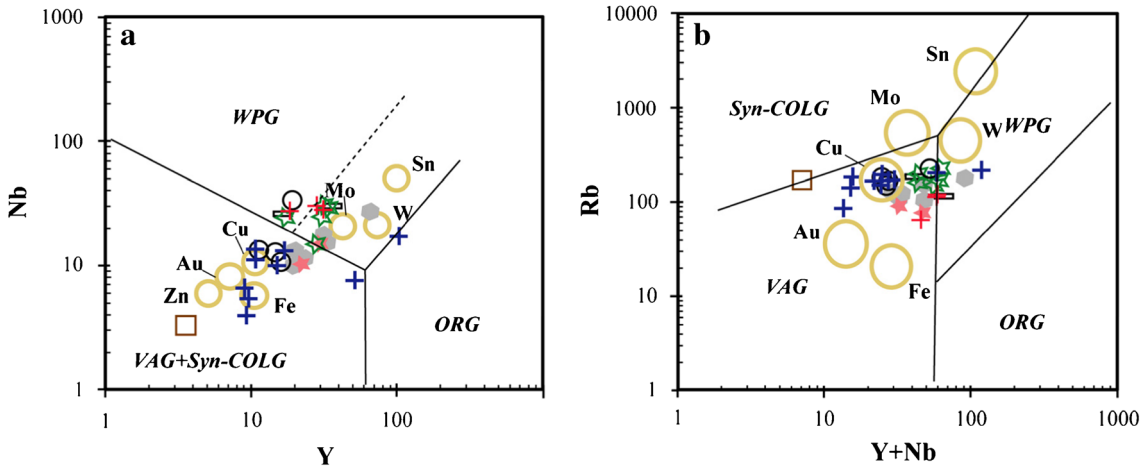

Fig.9 **a**, **b** Nb vs. Y and Rb vs. (Y + Nb) diagrams (Pearce et al. 1984; see also Förster et al. 1997); ORG = ocean-ridge granites; syn-COLG = syncollisional granites; VAG = volcanic arc granites; WPG = within-plate granites

plot nearby Cu, Fe, Au, Mo, W, and Zn skarn-related granitoids (Fig. 9). However, it should be noticed that samples plotting within the skarn-related granitoids domain in Fig. 2 are not necessarily the same exhibiting high contents in Cu, Pb, Th, and Zn. The most widespread skarn mineral observed in the studied sample is pyrite (not analyzed). This mineral occurs as disseminated small grains.

Thorium mineralization

Th mineralization occurs in the upper continental crust, particularly in placers, granitic rocks, or veins. The determination of the Th mineralizing potential and consequently the discrimination between unproductive and mineralized granitic rocks from Mbengwi was based on the analysis of their contents in P, followed by the use of the P_2O_5* 100/Th vs. B (B = Ti + Fe + Mg) diagram in accordance with Scheepers (2000).

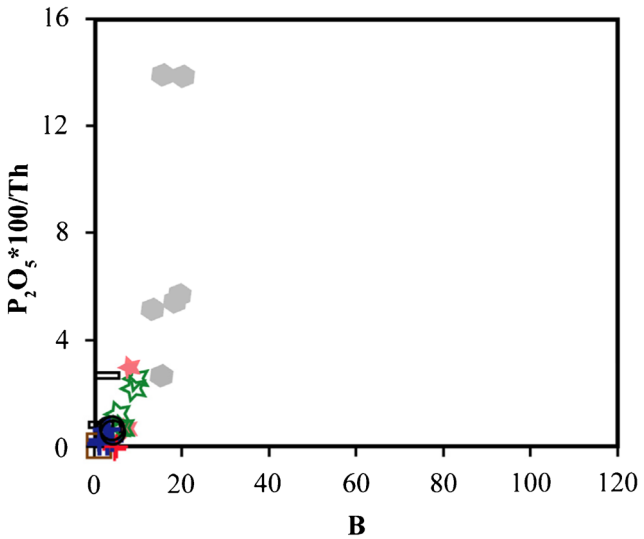

Fig. 10 Plots P_2O_5*100/Th versus B (B = Ti + Fe + Mg) for the Mbengwi granitoids

According to the previous author, Th-mineralized granitic rocks are particularly enriched in P/Th and their composition trend in the P_2O_5* 100/Th vs. B diagram is nearly parallel to the Y axis. The use of this diagram for the studied granitic rocks (Fig. 10) reveals that the general trend is almost vertical and that monzodiorites and monzonites are almost parallel to the Y axis and can therefore be considered as mineralized or potentially mineralized.

Conclusions

The calc-alkaline affinity alongside the I-type nature and the range of Sr/Y ratios of the Mbengwi granitoids evidence that their parental magmas particularly those of granites are likely fertile for Cu mineralization, related skarn, and for some metals, epithermal deposits. Nevertheless, they have not experienced post-magmatic hydrothermal activity required for Sn, U, W, or Ta mineralization, given that they are moderately differentiated and have high K/Rb ratios.

Several geochemical criteria such as color index, Rb/Sr, Ce/Yb, Sm/Eu, or Rb/Ba ratios in addition to the behavior of Rb, Ba, and Sr disclose the barren nature of the Mbengwi granitoids regarding Sn, and Mo; though they might be rather productive concerning Cu and mainly fertile regarding Zn, although we have not yet really observed minerals bearing those elements.

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