

The significance of carbonates in gold mineralization process of the Ashanti Gold Belt: Evidence from the country rocks of Ashanti and Prestea gold mines, Ghana

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Abstract

Mineralogical and textural changes which occurred in the country rocks (Sedimentary and volcanic rocks) following their deposition in the early Proterozoic resulted in the development of new minerals, disappearance of pre-existing minerals or recrystallization of the pre-existing minerals which led to the formation of siderite and ankerite among others. Electron microprobe analysis was carried out on carbonates in country rocks from Ashanti and Prestea mines of the Ashanti gold belt of the Birimian in southern Ghana. Results showed that the carbonates formed at about 350°C in the country rocks are probably related to hydrothermal activity which caused the alteration of these rocks. The alteration processes involved in the transformation were sulphidation, sericitization, rutile formation, silicification, carbonation, carbonitization and chloritization and some of these processes were related to major gold mineralization in the country rocks. The high content of Fe and Mg carbonates suggest the abundance and critical role of these minerals in the gold formation as this could be a factor in the abundance of Fe related minerals that contain gold in the country rocks.

Keywords: Alteration, siderite, ankerite, gold mineralization, Birimian, Ashanti, Prestea, Ghana

Introduction

Most of Ghana's economically viable mineral deposits including gold, bauxite, and manganese are hosted in the Paleoproterozoic Birimian sedimentary and volcanic rocks. The gold deposits and occurrences are largely associated with parallel northeasterly volcanic belts; namely the Kibi-Winneba, Ashanti, Sefwi, Bui, and Bole-Nangodi belts as well as the north-trending Lawra belt. The volcanic belts consist of low-grade metamorphosed basalts of originally predominantly tholeiitic composition (Abouchami et al. 1990) separated by basins consisting of isoclinally folded metasedimentary rocks composed of dacitic volcanoclastic rocks, wackes and volcanogenic argillites, which are derived from the belts (Leube et al., 1986, Abouchami et al., 1990, Lompo et al., 2009).

In the Birimian terrane, wall-rock alteration of the country rocks often took the form of pyritization, arsenopyritization, sericitization, chloritization, silicification and carbonitization and the processes or mechanisms responsible for these alterations and possible gold mineralization include hydrothermal activity, metamorphism and post-metamorphic deformation (Manu et al, 2013). The hydrothermal phase produced Fe- and Mg-rich chlorite, sulphide, sericite, siderite and ankerite, epidote and quartz during or after the prevalent metamorphism in the rocks (Manu et al, 2013). The Fe-rich carbonates form hydrothermal halos of variable sizes from few centimeters up to several tens of meters wide in wall rocks of gold deposits and occur in veinlets and disseminated throughout the ores (Mumin and Fleet, 1995).

The siderite and ankerite are carbonate mineralization which is usually associated with many mesothermal gold deposits of all ages worldwide, Phanerozoic (Sandiford and Keays, 1986; Panteleyev, 1990), Proterozoic (Leube et al., 1990; Leonardos et al., 1991; Mumin, 1994) and Archean (Colvine et al., 1988; Robert, 1991). In some places the carbonate minerals are primary constituents of the host and country rocks, or, more commonly, part of the secondary metamorphic mineral assemblage (Mumin and Fleet, 19995). Several research works have shown that compositional variations of individual carbonate phases are independent of changes in host rock, and vary little with pressure (Harker and Turtle, 1955; Goldsmith and Newton, 1969; Powell et al., 1984). The coexistence of some carbonate mineral pairs such as ankerite-siderite and calcite-dolomite indicate cation variations may be sensitive to a wide range of temperatures (i.e. 350 to 400°C), making them potentially useful as geothermometers (Harker and Turtle, 1955; Hutcheon and Moore, 1973; Nesbitt and Essene, 1982; Essene, 1983; Powell et al., 1984; Anovitz and Essene, 1987).

Carbonate minerals of siderite and ankerites commonly occur in all country rock as well as in mineralized rocks both in the altered and unaltered varieties. The siderites and ankerites commonly occur in a wide range of composition and this property make them potential indicator minerals for change in physical and chemical parameters during the evolution of the hydrothermal system. Previous research in lode gold deposits have concentrated on their fluid inclusion or stable isotope systematics and Mumin and Fleet, 1995 reported on the compositional variation and zoning of these carbonates and reconstructed the thermal and chemical evolution of the Bogosu-Prestea hydrothermal system. In this study, we present data on microprobe analysis of siderite and ankerite to get a closer understanding of the processes associated with gold mineralization in the Birimian.

Geological setting

Regional Geology

The Birimian of Ghana is made up of metasedimentary and metavolcanic rock units (Figure 1). The Birimian metasedimentary units consist of phyllites, hornblende-

actinolite schists, carbonate-chlorite schists and greywackes, and weakly metamorphosed tuffs, feldspathic sandstones and metamorphosed chemical sediments whilst the Birimian metavolcanic rocks contain most of metamorphosed rhyolitic and basaltic and andesitic lavas, minor amounts of metamorphosed rhyolitic and dacitic lavas and tuffs, Mn-rich and Si-rich chemical sediments also occur (Opere-Addo et al., 1993; Feybesse et al., 2006; Ibrahim et al., 2020; Sakyi et al., 2020; Sapah et al., 2021). Diabases and porphyries intrude the metavolcanic rocks (Eisenlohr, 1989; Nyame et al., 2020).

According to Ntiamoah-Agyakwa (1979), the Birimian rock unit about 10-15 km thick, generally dips to the southeast and is isoclinally folded. Two main types of granitoid intruded the Birimian. The Cape Coast type which is voluminous in mass, rich in aluminum (peraluminous) and intrudes the Birimian assemblage and the Dixcove granitoid type; smaller in mass and relatively Na-rich, may be contemporaneous with volcanism of the Birimian metavolcanics (Eisenlohr, 1989).

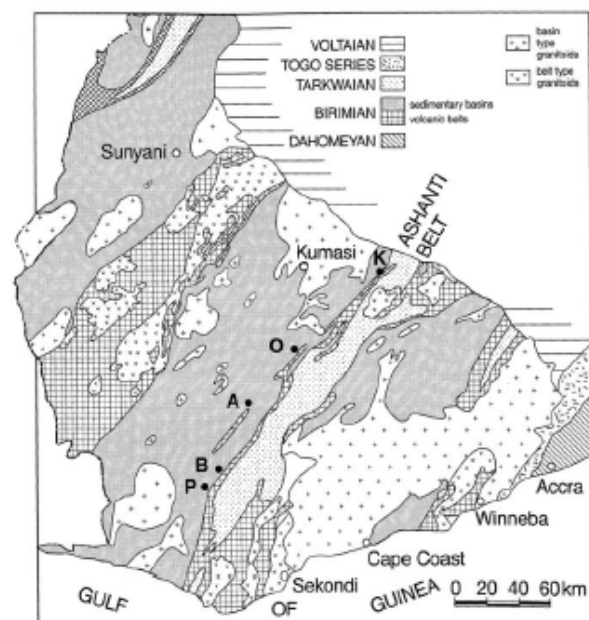


Figure 1: General geology of southern Ghana (after Leube and Hirdes, 1986, modified according to W. Hirdes and G. Loh, 1995). Locations of gold mines: K, Konongo;

O, Ashanti mine at Obuasi; A, Ayanfuri; B, Bogosu, and P, Prestea.

Local Geology

The Ashanti and Prestea mines are in a similar geological environment, the Ashanti belt. The Ashanti Belt generally assumes a synformal structure (Eisenlohr and Hirdes, 1992) and parts of the Birimian greenstones (metavolcanics/metavolcaniclastics) are overlain by a small unit of Tarkwaian metasedimentary rocks (Loh and Hirdes, 1996) which are intruded by mafic/ultramafic rocks (Dampare et al. 2008). The Birimian volcanic/volcaniclastic rocks and the mafic/ultramafic rocks were intruded by the Dixcove type granitoid (Opare-Addo et al., 1993; Feybesse et al., 2006).

According to Manu (1993), the metasedimentary rocks at both Ashanti and Prestea mines are mainly phyllites, metagreywacke and siliceous rocks. The phyllites megascopically, have a planar to crumple foliation. The evenly foliations with somewhat 'dull' lustre are pronounced in the grey-green to light green pure phyllite, ankerite phyllites and metagreywacke whereas the graphite phyllites, which is black in colour has a silky lustre (Manu, 1993). The phyllitic rocks, particularly the graphite ankerite phyllites occasionally contain millimeter big pyrites. The siliceous rock is black, hard and compact with foliation (Manu, 1993). The metavolcanic rocks are mainly metarhyolite. They are mainly grey-green, fine- to medium-grained, and massive and sometimes contain various sulphides including centimeter long arsenopyrite needles. The quartz reefs are grey, milky-white or glassy in colour.

Method

Fresh samples were taken from the Obuasi and Prestea mines and prepared into sections for microprobe analysis, using Cameca microbeam (Type Camebax MB) at the Geologische Institute, University of Hannover, Germany operated at a 15 KV accelerating voltage with 18 nA beam current.

Results and Discussion

Metamorphism of the country rocks

Mineralogical and textural changes occurred in the sedimentary and volcanic rocks following their deposition in the early Proterozoic. These changes were attained by the development of new minerals, the disappearance or recrystallization of the pre-existing minerals. Researchers have recognized contact and regional metamorphism in the Birimian. Local contact metamorphism (of the hornblende-hornfels facies) on the Birimian metavolcanic rocks caused predominantly by a tonalitic magma intrusion has been observed by Leube and Hirdes (1988) and is characterized by actinolite, epidote and albite minerals. Leube and Hirdes (1986) suggested that though the regional metamorphism grade varies between sub-greenschist (pumpellyite-prehnite) facies and amphibolite (almandine-amphibolite) facies, the bulk of the Birimian rocks is confined to the chlorite zone of the greenschist facies. Post-metamorphic shear zones have been recognized in the dormant and existing mines and can be interpreted as ductile to brittle deformation styles. Microscopically, the shear or deformation zones are characterized by elongate mineral grains or aggregate or deformed grains in the country rocks or differences in deformation intensity in the later formed quartz veins.

Hydrothermal alteration

Carbonates are widespread alteration minerals reported in the mines in Ghana and their formation is attributed to hydrothermal event. They are formed in S_2 and probably in pre- S_2 (i.e. S_1) deformation planes (Figure 2). This means that the formation conditions of the carbonates can be conveniently related to the hydrothermal event, which occurred after S_1 . Cooper (1934) and Afenya (1976) termed the carbonates at Prestea mine as ankerites and additional carbonate as siderite was found by Adjimah (1988). Similar carbonates reported at the Ashanti mine are ankerites and ferroan dolomite by Gyapong (1980) and siderite and ferroan dolomite by Hirdes and Leube (1989). Since the compound $\text{CaFe}(\text{CO}_3)_2$ does not exist (Reeder, 1983), phases with this molecule have been referred to by various writers as ankerites and ferroan dolomite because there are no strict rules. Using the

popular preference and suggestion by Reeder (1983) that the term ankerites be used for more Fe-rich phases and ferro and dolomite for less Fe-rich phases, the presented series here (i. e. the $\text{Ca}(\text{Fe,Mg})\text{CO}_3$ (see Table 1) are Fe-rich phases. Hence they are termed ankerites. Tables 1 and 2 show that the analysed carbonates are ankerites and siderite respectively, with slight enrichment in magnesium. The siderites tend to be more enriched in Mg than the ankerites. The reported carbonates at Prestea and Obuasi contrast slightly with those given here (Tables 1 and 2), due to the bulk analytical technique (namely X-ray diffraction and wet chemical methods) for the reported carbonates, which disregards textural and compositional differences compared to the electron microprobe analyses for those in Tables 1 and 3. The presence of the slightly enriched magnesium content in the siderites and ankerites is explained by the generally accepted complete substitution of Mg for Fe which exists in these minerals (Deer et al., 1963). The total carbonate composition (in mole %) was plotted in a triangular diagram in Figure 4. The siderites and ankerites show only little range in composition among themselves and no trend in composition towards one another (Figure 4). This suggests distinct generations for the carbonates. There are carbonates with “zoning” beside the homogeneous ones (e.g. 18/OB/310/6 in

Obuasi and 23/307/10 in Prestea). Microprobe analyses of one such “zoned” mineral (e.g. Mg-siderite in 18/OB/310/6 of Table 3) showed no chemical variations in MgO, FeO, CaO or MnO content between the core and the margin. The “zoned” appearance is probably due to the incorporation of carbonaceous materials in the core of the mineral during the early stages of their formation (Figure 3). This explanation is also supported by the fact that the “zoning” is more clearly seen microscopically when the carbonaceous material in the rock is high (compare 23/301/6 and 23/307/3). In Table 1, the maximum FeCO_3 content of the magnesian ankerite is less than 25 moles %. This corresponds to the experimental work by researchers such as Rosenberg (1967): Bickle and Powell, 1977; Powell et al. 1984, who found that ankerites with $\text{FeCO}_3 < 25$ mole % (MgCO_3 - and CaCO_3 - contents not given) are formed at about 350°C . Three samples (18/OB/310/6, 33/OB/138/10 and 23/301/6) have co-existing siderite and ankerites (Tables 1 and 2). The FeCO_3 mole content in the siderites suggest that the carbonates were formed at about 350°C . Since carbonates were also formed in S_1 and S_2 planes, the formation temperature at about 350°C for the carbonates is deduced to represent the temperature of the hydrothermal alteration event.

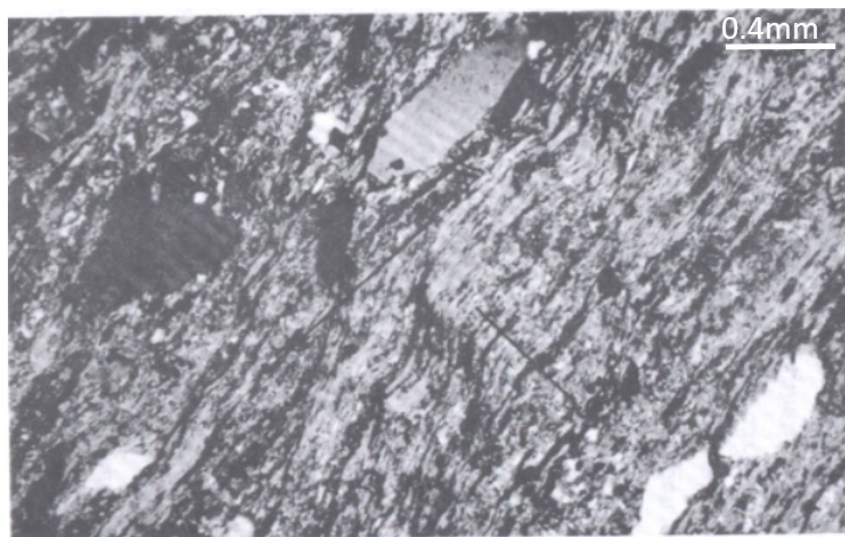


Figure 2: Photomicrograph of phyllite showing crenulation cleavage. Sample 38/OB/155/6

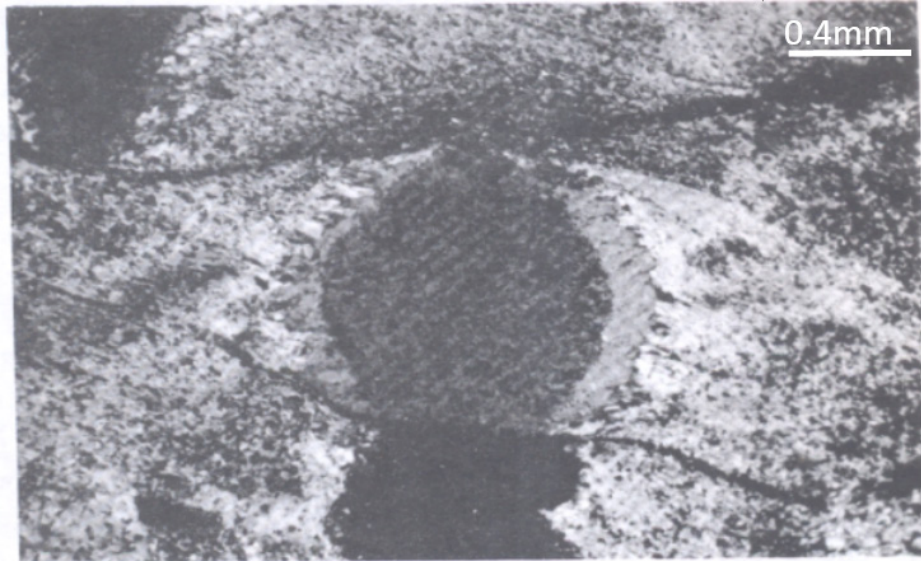


Figure 3: Porphyroblastic ankerite mottled at its core by opaques. Also at its margin are quartz and sericite intergrowth. Sample 23/308/4

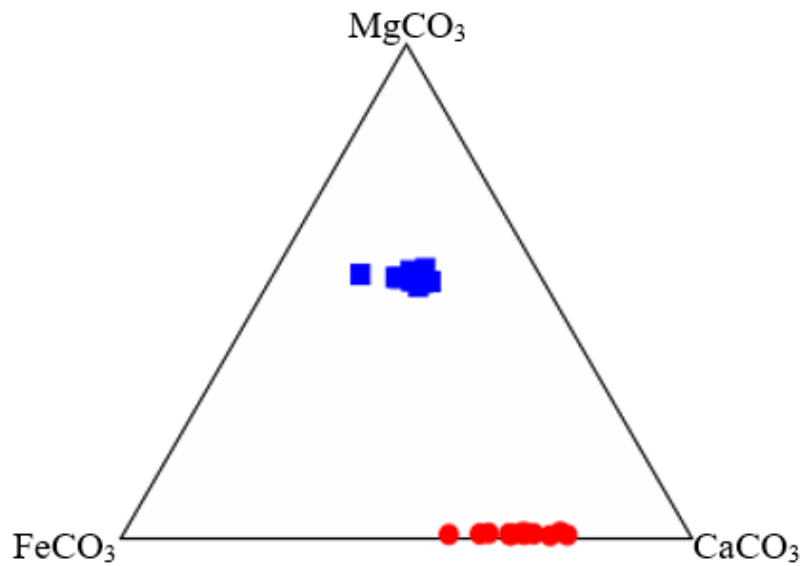


Figure 4: Analyses of carbonates from the country rocks in the system MgCO₃-FeCO₃-CaCO₃. ● Siderite and Ankerite ■

Table 1: Microprobe analyses of ankerites in country rocks from Ashanti and Prestea mines.

	33/ OB/10	18/OB/310/1				18/ OB/310/14			23/301/6		
FeO	14.56	17.12	14.82	16.85	15.58	16.13	16.61	18.16	16.44	9.95	13.78
MnO	0.29	0.31	2.3	0.66	0.59	0.06	0.62	0.67	0.46	0.58	0.46
MgO	11.73	10.57	10.19	9.79	10.61	10.51	9.07	9.28	10.36	14.76	11.78
CaO	29.62	28.65	29.53	28.28	28.4	29.08	30.47	29.18	29.21	29.74	28.966
SiO ₂	0.02	0	0.12	0.04	1.52	0	0.06	0	0.09	0.95	0.3
Al ₂ O ₃	0.01	0	0	0.05	0.02	0.04	0	0.02	0.02	0.01	0.1
*CO ₂	43.71	43.27	43.03	44.29	43.2	43.59	43.17	42.65	43.36	43.94	44.49
Sum	99.94	99.93	99.99	99.96	99.91	99.41	99.99	99.96	99.94	99.94	99.87
Wt%											
FeCO ₃	23.48	27.62	23.9	27.18	25.13	26.02	26.8	29.29	26.52	16.06	22.22
MnCO ₃	0.47	0.51	3.73	1.07	0.95	0.09	1	1.09	0.75	0.94	0.75
MgCO ₃	24.52	22.11	21.31	20.47	22.18	21.98	18.96	19.4	21.67	30.87	24.64
CaCO ₃	52.88	51.13	52.71	50.48	50.69	51.91	54.39	52.09	52.14	53.08	51.69
Mole%											
FeCO ₃	19.56	23.25	20.02	23.45	21.59	22.16	22.74	24.74	22.38	13.12	18.85
MnCO ₃	0.43	0.48	3.52	1.04	0.92	0.09	0.96	1.04	0.7	0.87	0.72
MgCO ₃	28.9	2.33	25.25	24.98	26.96	26.48	22.76	23.18	25.87	35.32	29.57
CaCO ₃	51.11	49.94	51.22	50.52	50.53	51.28	53.54	51.04	51.05	50.32	50.86
Cations											
Fe ²⁺	0.4	0.47	0.41	0.47	0.44	0.45	0.46	0.5	0.45	0.27	0.38
Mn ²⁺	0.01	0.01	0.06	0.02	0.02	0	0.02	0.02	0.01	0.02	0.01
Mg ²⁺	0.57	0.52	0.5	0.49	0.53	0.52	0.45	0.45	0.51	0.7	0.58
Ca ²⁺	1.03	1.01	1.04	1.02	1.02	1.03	1.08	1.03	1.03	1.02	1.03
Total	2.01	2.01	2.01	2	2.01	2	2.01	2	2	2.01	2

Total Fe as FeO

Table 2: Microprobe analyses of siderites in country rocks from Ashanti and Prestea mines.

	23/308/3		33/OB/138/12				23/301/6		33/OB/10	23/307/10	18/OB/310/1		
FeO	43	38.56	41.8	38.59	42.36	45.08	43.8	43.74	35.61	41.75	46.68	39.53	47.13
MnO	0.37	0.68	0.44	0.57	0.35	0.68	0.68	0.4	0.22	0.39	0.66	0.25	0.95
MgO	13.06	16.58	14.55	16.811	14.65	12.76	13.56	13.77	19.73	14.62	11.45	16.27	10.29
CaO	0.46	0.35	0.28	0.39	0.24	0.39	0.31	0.48	0.27	0.34	0.15	0.45	0.57
SiO ₂	0.54	0.03	1.15	0.78	1.12	0.76	0.12	0.04	0.1	0.69	0.09	0.3	0.04
Al ₂ O ₃	0.4	0	0.28	0.41	0	0.05	0.02	0	0.01	0.65	0.03	0.14	0
*CO ₂	42.04	43.73	41.47	42.07	41.23	40.24	41.31	41.57	44	41.33	40.94	42.99	40.96
sum	99.87	99.93	99.97	99.62	99.95	99.96	99.79	100	99.92	99.77	99.99	99.93	99.95
wt%													
FeCO ₃	69.36	62.19	67.42	62.24	68.33	72.71	70.64	70.55	57.43	67.34	75.29	63.77	76.02
MnCO ₃	0.6	0.68	0.72	0.93	0.57	1.1	1.1	0.65	0.35	0.63	1.06	0.41	1.55
MgCO ₃	27.31	16.58	30.42	35.5	30.63	26.69	28.35	28.8	41.25	30.57	23.94	34.03	21.52
CaCO ₃	0.82	0.35	0.5	0.69	0.43	0.69	0.56	0.85	0.48	0.61	0.27	0.79	1.02
Mole%													
FeCO ₃	63.27	54.93	60.69	54.68	60.69	54.68	64.63	62.72	62.43	60.13	68.03	56.29	69.49
MnCO ₃	0.6	1.1	0.72	0.92	0.72	0.92	1.1	1.1	0.65	0.63	1.08	0.41	1.59
MgCO ₃	35.24	43.33	38.08	43.7	38.08	43.7	33.56	35.61	36.05	38.61	30.61	42.5	27.83
CaCO ₃	0.9	0.64	0.51	0.7	0.51	0.7	0.71	0.58	0.87	0.63	0.28	0.8	1.08
Cations													
Fe ²⁺	1.3	1.11	1.22	1.11	1.23	1.31	1.27	1.26	1	1.22	1.37	1.14	1.4
Mn ²⁺	0.01	0.02	0.01	0.02	0.01	0.02	0.02	0.01	0.01	0.01	0.02	0.01	0.03
Mg ²⁺	0.69	0.85	0.76	0.86	0.76	0.66	0.7	0.71	1	0.76	0.6	0.84	0.55
Ca ²⁺	0.02	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.02	0.01	0.01	0.02	0.02

Total Fe as FeO

Table 3: Microprobe analyses of “zoned” siderite in country rock sample 18/OB/310/6

	Core		Margin	
FeO	47.29	46.57	45.96	45.96
MnO	0.76	0.78	0.29	0.15
MgO	11.32	11.5	11.96	12.13
CaO	0.33	0.47	0.61	0.52
SiO ₂	0.02	0.02	0.27	0.13
Al ₂ O ₃	0	0	0.04	0
*CO ₂	40.23	40.64	40.76	40.98
Sum	99.95	99.96	99.89	99.87
Wt%				
FeCO ₃	76.28	75.11	74.14	74.14
MnCO ₃	1.24	1.27	0.46	0.24
MgCO ₃	23.67	24.04	25.02	25.36
CaCO ₃	0.58	0.83	1.09	0.93
Mole %				
FeCO ₃	68.2	67.35	66.6	71.24
MnCO ₃	1.25	1.28	0.47	0.27
MgCO ₃	29.95	30.5	31.14	27.46
CaCO ₃	0.61	0.87	1.14	1.04
Cations				
Fe ²⁺	1.38	1.36	1.35	1.34
Mn ²⁺	0.02	0.02	0.01	0
Mg ²⁺	0.59	0.6	0.62	0.63
Ca ²⁺	0.01	0.02	0.02	0.02
Sum	2	2	2	1.99

Total Fe as FeO

Gold mineralization

Petrographic investigation by Manu et al. (2013) suggests that the metasedimentary and metavolcanic rocks in the Birimian gold belt are transformed mainly by metamorphism and to a lesser extent by hydrothermal activity. The alteration processes involved are silicification, sulphidation, rutile-formation, sericitization, carbonation, and different stages of chloritization and some of these processes are related to the main gold mineralization in the country rocks. Several works elsewhere (e.g. Kiefer, 2004) have shown the importance of carbonate formation in gold mineralization. For example, high CO₂ content in hydrothermal fluid has been shown to aid in the formation of ferroan dolomite associated with gold mineralisation (e.g. for Golden Mile deposit; Philips & Brown, 1987 and Blue Dot Mine; Adomako-Ansah et al., 2013). From this study, the abundance of carbonate minerals (ankerites and siderites) in the Birimian formed at about 350°C gives further indication of high CO₂ content in the hydrothermal fluid that deposited the gold and this suggestion is further buttressed by fluid inclusion studies at Ashanti, Prestea and Mpesatia gold mines in Ghana that have indicated the abundance of high CO₂ content in the gold mineralization fluids (e.g. Manu, 1993; Leube and Hirdes, 1990). Zoned siderite (Table 3) showed enrichment in Fe and this composition indicates Fe substitution among other minerals and that gold mineralization and the carbonate alteration might not have been in a stable phase with the ore-bearing fluid.

Implications of carbonates for gold exploration

Major gold deposits found in the Ashanti belt of the Birimian of southwestern Ghana have been found to be associated with arsenopyrite, chalcopyrite and pyrite (Dzigbodi-Adjimah, 1993) and these minerals have been used as pathfinders which have led to exploration success in the Birimian of southwestern Ghana. Since from this study, the sulphides together with the carbonates (siderites and ankerites) were produced by the same hydrothermal activity which brought about the gold mineralization, the carbonates could be a useful guide

and could be employed in existing mines and for future exploration work in the Ashanti belt and the Birimian of Ghana in general.

Conclusion

From the study, carbonates in the country rocks of Ashanti and Prestea mines in the Ashanti gold belt of the Birimian of Southern Ghana can be related to hydrothermal activity. The hydrothermal activity altered the country rocks and introduced the carbonates, and this carbonitization process is related to the main gold mineralization in the country rocks. Other alterations caused by the hydrothermal activity which led to the gold mineralization include sulphidation, carbonation and chloritization. It can therefore be said that the carbonates and gold were deposited under similar conditions as those of the hydrothermal activity.

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Conflict of interest

The authors declare that they have no competing interests.

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