Research Article

First Report of Florencite from the Singhbhum Shear Zone of the East Indian Craton

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Metamorphic florencite is being reported from kyanite-rich rocks from the eastern part of the Palaeo- to Mesoproterozoic Singhbhum shear zone. This is the first report of florencite from the Precambrian rocks of the Indian Shield. Host rock of florencite is a kyanite-rich rock (>80 vol%) with small and variable amounts of quartz, lazulite, augelite, and rutile. Florencite forms small (<20 microns) idioblastic-to-subhedral crystals that are included in large kyanite grains. Rarely, florencite replaces kyanite. The florencite has small proportion of crandallite (8.7–11.8 mol%) and goyazite (<2 mol%) components. Florencite of this study is dominated by Ce (~49 mol%) with significant La (~30 mol%) and Nd (~21 mol%). Compared to other florencite occurrences of the world, florencite of the studied rock is impoverished in S, Sr, and Ba and rich in P. Stability of the assemblage florencite-kyanite-augelite-lazulite and the quantitative thermobarometry in the adjoining rocks suggest that florencite was formed during Palaeoproterozoic metamorphism that culminated at the P - T range of $490 \pm 40^\circ\text{C}$ and 6.3 ± 1 kbar. Integrating all the geological features it is postulated that florencite was formed due to metasomatism of some aluminous protolith by infiltration of acidic fluids charged with PO_4^{-3} and LREE.

1. Introduction

Florencite is a rare but important mineral in the alunitic super group with the general formula of $\text{AB}_3(\text{XO}_4)_2(\text{OH})_6$, where A-site filled with Ce, La, and Nd, B-site with Al and X-site with P (Bayliss et al. [1]). The structure of florencite also accommodates variable amounts of Ca^{2+} , Pb^{2+} , Hg^{2+} , K^+ , Ba^{2+} , Sr^{2+} , Rb^+ (in A-site), Fe^{3+} , Cu^{2+} , Zn^{2+} , Sn^{2+} , V^{3+} , Cr^{3+} , and Ga^{3+} (in B-site) (Bayliss et al. [1], Dill [2]). Florencite is commonly associated in hydrothermally altered rock (Dill [2], Gaboreau et al. [3], Hikov et al. [4], and Repina [5], among others) and less commonly in metamorphic rocks (Nagy et al. [6], Izbrodin et al. [7], and Janots et al. [8]). Because of its open structure that can accommodate a large number of cations and anions including the REE, the composition of florencite provides a wealth of information about the source and composition of the metamorphic and hydrothermal fluids (Visser et al. [9], Nagy et al. [6], Dill [2], Gaboreau et al. [3], Hikov et al. [4], Izbrodin et al. [7],

Repina [5], and Janots et al. [8]). Once formed florencite is very difficult to be destroyed even in the weathering profile and hence controls the mobility of LREE over a wide range of geological conditions (Gaboreau et al. [3], Izbrodin et al. [7], and Repina [5]). Florencite is associated with different types of hydrothermal or deposits including unconformity type uranium deposits and thus the presence of this mineral can be used as a pathfinder mineral in exploration of these deposits (Gaboreau et al. [3]).

Singhbhum shear zone (SSZ) of the East Indian shield separates the Palaeo- to Meso- to Neo Archaean Singhbhum craton from Palaeoproterozoic metamorphosed volcano sedimentary pile, known as North Singhbhum Fold Belt (NSFB, Figure 1 after Dunn and Dey [10] and Saha [11]). It is generally agreed upon that Palaeoproterozoic tectonism led to thrusting of the NSFB over the Archaean Singhbhum craton along the SSZ (discussed in Sarkar and Gupta [12]). Multitudes of rocks are intermingled, intensely sheared and hydrothermally altered along the SSZ. Repeated

FIGURE 1: Geologic map showing the distribution of stratigraphic units in a part of eastern India. After Dunn and Dey [10] and Saha [11]. SSZ: Singhbhum shear zone, NSFB: North Singhbhum Fold Belt, IOG: Iron Ore Group. The rectangle around Kanyaluka (marked by red asterisk) is blown up in Figure 2.

hydrothermal activities developed different types of Cu-Fe-U-P deposits that are associated with tourmalinization, muscovitization, and ferruginization (discussed in Sengupta et al. [13], and Sarkar and Gupta [12]). Infiltration-driven metamorphism in the SSZ produced a number of exotic rocks including per-aluminous kyanite-quartz rocks that fringe the northern boundary of the SSZ (Figures 1 and 2; Figure 2: partly after Mukhopadhyay and Deb [14]). In the eastern part, where the SSZ takes a bend towards south (Figure 1), kyanite-quartz rock is spatially associated with chloritoid-bearing schist, psammopelites, mica schist, and bands of tourmalinite (Figure 2). All these rocks share a common history of deformation and metamorphism that culminated at $490 \pm 40^\circ\text{C}$ and $6.3 \pm 1\text{ kbar}$ (Sengupta [15]). In this communication, we are describing the mode of occurrence of florencite in the host of kyanite-rich rock (>80 vol% kyanite) that is exposed near the village of Kanyaluka (Figure 2). Integrating all the petrological data we demonstrate that florencite was developed due to infiltration of acidic fluid charged with P and LREE into the per-aluminous kyanite-rich rock at the culmination of metamorphism and deformation. Incidentally, this is the first report of florencite from any Precambrian rocks of India.

2. Petrography and Mineral Chemistry

In domains of minimum strain, kyanite-rich rock develops randomly oriented blades of kyanite that occupy more than 80 vol% of the rock (Figure 3(a), abbreviations after Kretz [16]). Grains of quartz and rutile occupy the interstitial space of the mesh formed by the kyanite blades (Figures 3(a) and 3(b)). The kyanite-rich rock develops centimeter to decimeter thick bands of intense shearing. In the shear bands, kyanite blades are kinked, bent, and fractured (Figure 3(b)) and the quartz grains show undulose extinction. Locally, deformed kyanite blades are extensively replaced by augelite and lazulite (Figure 4(a)). Unlike kyanite, lazulite and augelite do not show any deformation (static growth). In the backscattered electron (BSE) images, florencite grains appear as numerous small bright spots in the dull background composed of lazulite, kyanite, and quartz (Figure 4(b)). Small disseminated idioblastic, subhedral to anhedral crystals (<20 microns) of florencite are included in kyanite, quartz, and lazulite (Figures 4(c) and 4(d)). Rarely, florencite replaces kyanite (Figure 4(c)). Textural features attest to the view that florencite crystals are left stranded within lazulite when the latter mineral replaced kyanite (Figure 4(d)). This feature suggests equilibrium coexistence of florencite and lazulite.

FIGURE 2: Lithological map of the South Eastern sector of Singhbhum shear zone (SSZ) around Kanyaluka. (Partly after Mukhopadhyay and Deb [14]). The location from where the samples have been collected is marked with red asterisk.

FIGURE 3: (a) Randomly oriented kyanite grains forming a mesh-like appearance. Some corroded rutile grains and quartz are also seen in the interstitial spaces and (b) Kyanite poor zone in the host rock showing the presence of deformed (kinked) kyanite. Mineral abbreviations used are after Kretz [16].

FIGURE 4: BSE images showing (a) Kyanite blades replaced by augelite and lazulite, (b) overall view of the lazulite rich zone: relicts of kyanite showing corroded boundary are sparsely distributed here. The small bright spots seen here are florencite. (c) florencite grain with protruding grain boundary inside kyanite, showing that florencite replaces kyanite, (d) florencite grain stranded within lazulite. Aug: augelite. Fl: florencite. All other mineral abbreviations are after Kretz [16].

Electron microprobe analyses and WDS spectrum of the florencite are presented in Table 1 and Figure 5, respectively. Also included in Table 1 are the representative analyses of kyanite, lazulite, and rutile. For comparison, florencite analyses from some well-known localities are also included in Table 1. Chemical compositions of florencite and the adjacent minerals were determined from carbon-coated thin sections by electron microprobe analysis (EMPA) with a CAMECA SX100 electron microprobe at the Central Petrological Laboratory, Geological Survey of India, Kolkata. For elements other than Sr, Ba, and the REE, the accelerating voltage used was 15 kV with a 12 nA current. Elements were analyzed using natural standards, except for Mn and Ti for which synthetic standards were used. For the heavy metals (Ba, Sr, and REE) 20 kV and 20 nA were used. The following standards are used for REE (REE glass), Sr (celestite), and Ba (barite). The raw data were processed using the PAP procedure (Pouchou and Pichoir [17]). The composition of florencite is recalculated on 11 oxygen basis and the nomenclature of the different species is according to Bayliss et al. [1]. Compositionally florencite is essentially a solid solution of the species Florencite-(Ce) (48.7 mol%), Florencite-(La) (29.9 mol%), and Florencite-(Nd) (21.3 mol%) (Table 1). Similar to other natural florencite compositions, concentrations of LREE

outweigh the concentrations of HREE. The concentrations of HREE, S, and As are below the detection limit of electron microprobe. Concentrations of Sr (0.002 to 0.008 apfu), Ba (~0.00003 apfu), Ca (0.040 to 0.062 apfu), and K (0.001 to 0.012 apfu) are low. Concentration of ThO₂ varies between ~0.5 and 1.2 wt% (0.01–0.024 apfu). The WDS spectrum suggests that the elements that are not measured do not have any significant concentrations. Lazulite is dominated by Mg (98.06 mol% lazulite) with a small amount of scorzalite (1.94 mol% Fe-Lazulite, Table 1). Kyanite, rutile, and quartz have essentially the end member compositions.

Entry of small amount of Th and Ca in the structure of florencite can be explained by the substitution $\text{REE}^{3+} \leftrightarrow \text{Th} + \text{Ca}$ (Nagy et al. [6], Georgieva and Velinova [18], and Gaboreau et al. [3]). Compared to the florencite compositions reported from many florencite occurrences in the world, florencite compositions of this study are depleted in Sr, Ca, Ba, and S whereas they are enriched in P₂O₅ (Table 1).

3. Discussion

Florencite in the kyanite rich rock of the Singhbhum shear zone records the first occurrence of this mineral from any

TABLE 1: Representative analyses of florencite, lazulite, augekite, kyanite, and rutile mineral from studied area. Florencite mineral composition has been compared with compositions from different localities.

Elements	Florencite (calculated on II oxygen basis. Values in wt%)		Location						
			Florencite data by Nagy et al. 2002 [6] (values in wt%)	Florencite data by Janots et al. 2006 [8] (values in wt%)	Florencite data by Doroshkevich et al. 2009 [19] (values in wt%)	Lazulite (values in wt%)	Augelite (values in wt%)	Kyanite (values in wt%)	Rutile (values in wt%)
Singhbhum shear zone (SSZ)									
			Sopron Hills, Eastern Alps, Hungary	Sebtide complex, Rif, Morocco	Amba-Dongar, Gujarat, India				
SiO ₂	0.00	0.06	n.a.	0.24–4.2	>0.75	0.01	0.23	36.69	0.00
TiO ₂	0.07	0.00	n.a.	n.a.	n.a.	0.03	0.06	0.02	100.90
Al ₂ O ₃	28.47	27.37	28.66–31.89	27.10–31.92	27.86–30.67	33.49	49.30	62.45	0.06
Cr ₂ O ₃	0.00	0.00	n.a.	n.a.	n.a.	0.00	0.08	0.04	0.13
FeO	0.00	0.01	n.a.	0.17–1.4	n.a.	0.00	0.00	0.03	0.10
MnO	0.00	0.00	n.a.	n.a.	n.a.	0.43	0.04	0.02	0.00
CaO	0.42	0.64	0.72–1.44	0.42–0.69	0.23–0.81	0.01	0.00	0.00	0.01
MgO	0.01	0.05	n.a.	0.02–0.70	n.a.	13.32	0.03	0.01	0.00
Na ₂ O	0.09	0.09	n.a.	0.01–0.06	n.a.	0.03	0.00	0.06	0.00
K ₂ O	0.00	0.00	n.a.	n.a.	n.a.	0.00	0.00	0.02	0.01
P ₂ O ₅	30.81	30.72	26.97–28.93	22.4–26.4	26.08–28.56	48.44	37.09	0.00	0.00
ZrO ₂	0.00	0.00	n.a.	n.a.	n.a.	—	—	—	—
Nb ₂ O ₅	0.00	0.00	n.a.	n.a.	n.a.	—	—	—	—
La ₂ O ₃	6.83	7.69	6.46–8.66	4.22–4.25	3.91–12.64	—	—	—	—
Ce ₂ O ₃	10.93	12.15	10.91–14.33	8.37–9.26	4.94–12.32	—	—	—	—
PbO	0.00	0.00	n.a.	n.a.	n.a.	—	—	—	—
ThO ₂	0.49	1.18	0.55–9.94	0.59–1.09	n.a.	—	—	—	—
U ₂ O ₃	0.04	0.02	n.a.	0.07–0.17	n.a.	—	—	—	—
BaO	0.00	0.00	n.a.	n.a.	n.a.	—	—	—	—
SrO	0.12	0.15	0.16–0.67	1.32–5.91	4.47–13.36	—	—	—	—
Nd ₂ O ₃	2.70	2.61	1.65–5.00	3.96–4.80	1.02–2.91	—	—	—	—
Sm ₂ O ₃	1.10	1.06	0.10–0.92	0.55–0.60	n.a.	—	—	—	—
SO ₃	0.00	0.00	n.a.	0.21–0.59	1.08–4.71	—	—	—	—
Total	82.08	83.81	87.69–90.36	78.21–86.35	71.40–78.98	95.76	86.83	99.40	101.25
	a.p.f.u.	a.p.f.u.	a.p.f.u.	a.p.f.u.	a.p.f.u.	a.p.f.u.	a.p.f.u.	a.p.f.u.	a.p.f.u.
Si	0.00	0.01	n.a.	0.020–0.379	0.060–0.170	0.00	0.02	1.00	0.00
Ti	0.00	0.00	n.a.	n.a.	n.a.	0.00	0.00	0.00	1.00
Al	2.99	2.90	3.203–3.360	2.880–3.131	2.710–2.950	1.95	3.84	2.00	0.00
Cr	0.00	0.00	n.a.	n.a.	n.a.	0.01	0.00	0.00	0.00
Fe	0.00	0.00	n.a.	0.012–0.107	0.020–0.333	0.02	0.00	0.00	0.00
Mn	0.00	0.00	n.a.	n.a.	n.a.	0.00	0.00	0.00	0.00
Ca	0.04	0.06	0.068–0.105	0.038–0.067	0.020–0.070	0.00	0.00	0.00	0.00
Mg	0.00	0.01	n.a.	0.003–0.095	n.a.	0.98	0.00	0.00	0.00
Na	0.02	0.02	n.a.	0.002–0.012	n.a.	0.00	0.00	0.00	0.00
K	0.00	0.00	n.a.	n.a.	n.a.	0.00	0.00	0.00	0.00

TABLE I: Continued.

Elements	Singhbhum shear zone (SSZ)			Location					Rutile (values in wt%)
				Florence data by Nagy et al. 2002 [6] (values in wt%)	Florence data by Janots et al. 2006 [8] (values in wt%)	Florence data by Doroshkevich et al. 2009 [19] (values in wt%)	Lazulite (values in wt%)	Augelite (values in wt%)	
				Sopron Hills, Eastern Alps, Hungary	Sebtide complex, Rif, Morocco	Amba-Dongar, Gujarat, India			
P	2.33	2.34	2.35	2.041–2.117	1.710–1.863	1.770–2.001	2.03	2.08	0.00
Zr	0.00	0.00	0.00	n.a.	n.a.	n.a.	—	—	—
Nb	0.00	0.00	0.00	n.a.	n.a.	n.a.	—	—	—
La	0.11	0.13	0.12	0.104–0.106	0.131–0.140	0.110–0.340	—	—	—
Ce	0.18	0.20	0.19	0.204–0.213	0.277–0.282	0.140–0.392	—	—	—
Pb	0.00	0.00	0.00	n.a.	n.a.	n.a.	—	—	—
Th	0.01	0.02	0.02	n.a.	0.022–0.011	n.a.	—	—	—
U	0.00	0.00	0.00	n.a.	0.001–0.004	n.a.	—	—	—
Ba	0.00	0.00	0.00	n.a.	n.a.	n.a.	—	—	—
Sr	0.01	0.01	0.01	0.011–0.035	n.a.	n.a.	—	—	—
Nd	0.09	0.08	0.09	0.142–0.156	0.128–0.143	0.030–0.071	—	—	—
Sm	0.03	0.03	0.03	0.023–0.027	0.018–0.019	n.a.	—	—	—
S	b.d.l.	b.d.l.	b.d.l.	n.a.	0.069–0.285	0.070–0.273	—	—	—
Total cation	5.80	5.80	5.79	5.892–5.992	5.763–5.945	5.637–5.834	4.98	5.95	3.00
ΣREE	0.42	0.45	0.44	0.484–0.537	0.603–0.612	0.300–0.603			1.00
Florence (mol%)	89.94	86.69	88.45						
Goyazite (mol%)	1.36	1.47	1.03						
Crandallite (mol%)	8.70	11.84	10.52						

Note n.a.: not available; b.d.l.: below detection limit.

FIGURE 5: WDS of florencite showing Al, P, Ce, and La. TAP and PET are crystals of the electron microprobe machine.

Precambrian rocks of the peninsular India. The only other locality of florencite in India is the carbonatite complex of Amba Dongar, Gujarat (Doroshkevich et al. [19]).

Textural features suggest that florencite was formed during and after the growth of kyanite and, hence, originated during metamorphism that accompanied the ductile shearing of the studied rock. Florencite remained stable during the formation of lazulite and augelite that replaced kyanite under static condition (post-shearing). Experimental study in the Al-P-O-H system and the observations from natural rocks show that the assemblage augelite + kyanite is stable at conditions 380°–475°C and pressure >2 kbar (Wise and Loh [20] and Visser et al. [9]). The assemblage kyanite + lazulite, on the other hand, has a wide thermal and baric stability (>400°C and >2 kbar, Schmid-Beurmann et al. [21] and Morteani et al. [22]). Stability of florencite at high temperature (up to 550°C) is reported from the eastern Alps (Nagy et al. [6]) and from African carbonatites (Mckie [23]). Briefly, the assemblage kyanite + augelite + lazulite + florencite appears to form at temperature and pressure that exceeded 400°C and 2 kbar. This is in a good agreement with the calculated P - T values of $490 \pm 40^\circ\text{C}$ and $\sim 6 \pm 1$ kbar from the adjoining chloritoid garnet bearing schist (Sengupta [15]).

Origin of florencite in kyanite-quartz rock requires advective transport of LREE and P presumably by infiltration of aqueous fluids. Singhbhum shear zone is characterized by repeated infiltrations of aqueous fluids that resulted in mineralization of Cu-Fe-U-P and tourmalinization (reviewed in Sengupta et al. [13] and Sarkar and Gupta [12]). In this study we document phosphate, REE and Mg-metasomatism, which developed end member lazulite (very low content of scorzalite) in kyanite-rich rock. Several studies have demonstrated that florencite develops in hydrothermally altered (*sensu lato*) rock in which the metasomatic fluids are oxidized and have acidic pH (Visser et al. [9], Nagy et al. [6], Gaboreau

et al. [3], Hikov et al. [4] and Georgieva and Velinova [18]). In view of this we envisage that infiltration of acidic fluid from an extraneous source to be responsible for the development of florencite. Absence of muscovitization of kyanite in kyanite quartz rock of this particular studied area and extensive tourmalinization of the adjoining rocks (Sengupta et al. [13]) supports that acidic metasomatic fluids infiltrated the rocks of the area. Studies have shown that acidic fluids can dissolve a large amount of PO_4^{3-} and LREE as these chemical species form the ligand $(\text{REE}(\text{PO}_4)_{\text{aq}})$ (Ayers and Watson [24], *c.f.* Jones et al. [25]). This fluid upon interacting with per-aluminous host rock stabilized florencite (Nagy et al. [6]).

4. Conclusion

- (1) Florencite, a REE-Al phosphate, has been reported from a metamorphosed kyanite-rich rock from the Singhbhum shear zone of the east Indian Shield.
- (2) Petrology of the florencite-bearing mineral association suggests metamorphic growth of florencite in the P - T range of $\sim 6 \pm 1$ kbar and $490^\circ \pm 40^\circ\text{C}$. This is the first report of florencite from Precambrian rocks of India.
- (3) Florencite was formed due to interaction of acidic aqueous fluids charged with PO_4^{4-} and REE and aluminous country rock during regional metamorphism and ductile shearing in the Singhbhum shear zone.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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