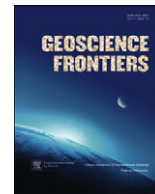


Contents lists available at [SciVerse ScienceDirect](http://www.elsevier.com/locate/gsf)

China University of Geosciences (Beijing)

Geoscience Frontiers

journal homepage: www.elsevier.com/locate/gsf

Research paper

REE geochemistry of auriferous quartz carbonate veins of Neoproterozoic Ajjanahalli gold deposit, Chitradurga schist belt, Dharwar Craton, India

S. Sarangi^{a,*}, R. Srinivasan^b, V. Balaram^c^a Department of Applied Geology, ISM-Dhanbad, India^b 114, Kshithija, Ramanashree Nagar, Bannerghatta Road P.O., Bangalore 560 076, India^c National Geophysical Research Institute (Council of Scientific and Industrial Research), Hyderabad 500 007, India

ARTICLE INFO

Article history:

Received 29 August 2012

Received in revised form

13 November 2012

Accepted 26 November 2012

Available online 20 December 2012

Keywords:

U-shaped REE pattern

Eu anomaly

Quartz carbonate veins (QCVs)

Orogenic gold deposits

Dharwar Craton

ABSTRACT

REE composition of the carbonates of the auriferous quartz carbonate veins (QCVs) of the Neoproterozoic Ajjanahalli gold deposit, Chitradurga schist belt, Dharwar Craton, is characterized by U-shaped chondrite normalized REE patterns with both LREE and HREE enrichment and a distinct positive Eu anomaly. As positive Eu anomaly is associated with low oxygen fugacity, we propose that the auriferous fluids responsible for gold mineralization at Ajjanahalli could be from an oxygen depleted fluid. The observed positive Eu anomaly is interpreted to suggest the derivation of the auriferous fluids from a mantle reservoir. The location of Ajjanahalli gold deposit in a crustal scale shear zone is consistent with this interpretation.

© 2012, China University of Geosciences (Beijing) and Peking University. Production and hosting by Elsevier B.V. All rights reserved.

1. Introduction

Epigenetic Archean orogenic gold deposits occur in quartz carbonate veins (QCVs) or as disseminations in crustal scale shear zones (Groves et al., 1988, 2003). So far, more than 100 deposits of this nature have been reported in different parts of the world (Goldfarb et al., 2005). From the field, petrographic, geochemical and fluid inclusion studies, it has been shown that gold in this deposit is carried in low salinity, H₂O–CO₂ ± CH₄ ± NaCl rich hydrothermal fluids (Goldfarb et al., 2005) in a pH range of 5–6 and redox control by HSO₄/H₂S and CO₂/CH₄ buffer (Mikucki and Ridley, 1993). The fluid transports gold, as a reduced sulfur complex (Groves et al., 2003). Redox calculations of alteration assemblages show that most

deposits formed by relatively reduced ore fluids, are characterized by assemblages pyrite ± arsenopyrite ± stibnite in the lowest temperature of sub-greenschist facies; pyrite ± arsenopyrite ± pyrrhotite at intermediate temperature greenschist to low amphibolites facies and loellingite ± arsenopyrite ± magnetite ± ilmenite ± pyrrhotite in high-temperature conditions of amphibolite-granulite facies (Mikucki and Ridley, 1993). However, some deposits formed from relatively oxidized fluids are characterized by assemblages containing magnetite or hematite at low to intermediate temperatures and pyrrhotite ± pyrite ± chalcopyrite ± ilmenite ± spinel assemblage at high temperature. In general, high-temperature deposits appear to have formed at high values of $f(O_2)$.

HFSE (Th, Nb, Ta, Zr, Hf, Ti, Y, P, Al, Ga), REE and compatible elements such as Sc and V are usually alteration insensitive (Kerrich, 1983; McCuaig and Kerrich, 1998). Most deposits are characterized by enrichments of associated elements such as As, Sb, Se, Te, Bi, W and B, LILE (K, Rb, Ba, Li, Cs, Tl) and volatiles (H₂O, CO₂, CH₄ and H₂S) as suggested by Kerrich (1983) and references therein. Other major elements, such as Fe, Mg, Ca and Na are variably added or depleted depending on the bulk composition of host lithology (Kerrich, 1983).

In spite of having many characters in common, gold deposits differ in terms of their economic viability from world class to prospect level. Source of the gold mineralizing fluids has been

* Corresponding author. Tel.: +91 0326 2235763; fax: +91 0326 2296616.

E-mail addresses: ssarangi2@rediffmail.com (S. Sarangi), srinimalu@gmail.com (R. Srinivasan).

Peer-review under responsibility of China University of Geosciences (Beijing).



Production and hosting by Elsevier

a subject of debate. Mantle, felsic magma, lamprophyre melts, circulating metamorphic and meteoric waters have all been suggested (Kerrick and Fyfe, 1981; Burrows et al., 1986; Groves et al., 1988; Nesbitt, 1988; Rock et al., 1989; Ridley and Diamond, 2000).

The Neoproterozoic Dharwar greenstone belts in the Dharwar Craton of southern India host a number of orogenic type gold prospects and a few deposits that include a couple which are world class deposits, namely the Kolar and Hutti gold deposits. Smaller deposits which have been mined are at Bellara, Ajjanahalli, G.R. Halli and Gadag. About 26 gold prospects occur in a 400 km long

crustal scale shear zone along the eastern margin of the Chitradurga greenstone belt in the Dharwar Craton including the Ajjanahalli and G.R. Halli deposits that produced gold for about a decade. Recently, based on C and O isotope studies of carbonates of the auriferous quartz carbonate veins, Sarangi et al. (2012) assigned magmatic/mantle source for the mineralizing fluids that gave rise to Ajjanahalli and G.R. Halli deposits in common with world class Kolar gold deposit (cf. Santosh, 1992). In this work, we examine REE characters of the same carbonates from the Ajjanahalli deposit to constrain redox conditions as well as source of the auriferous fluids.

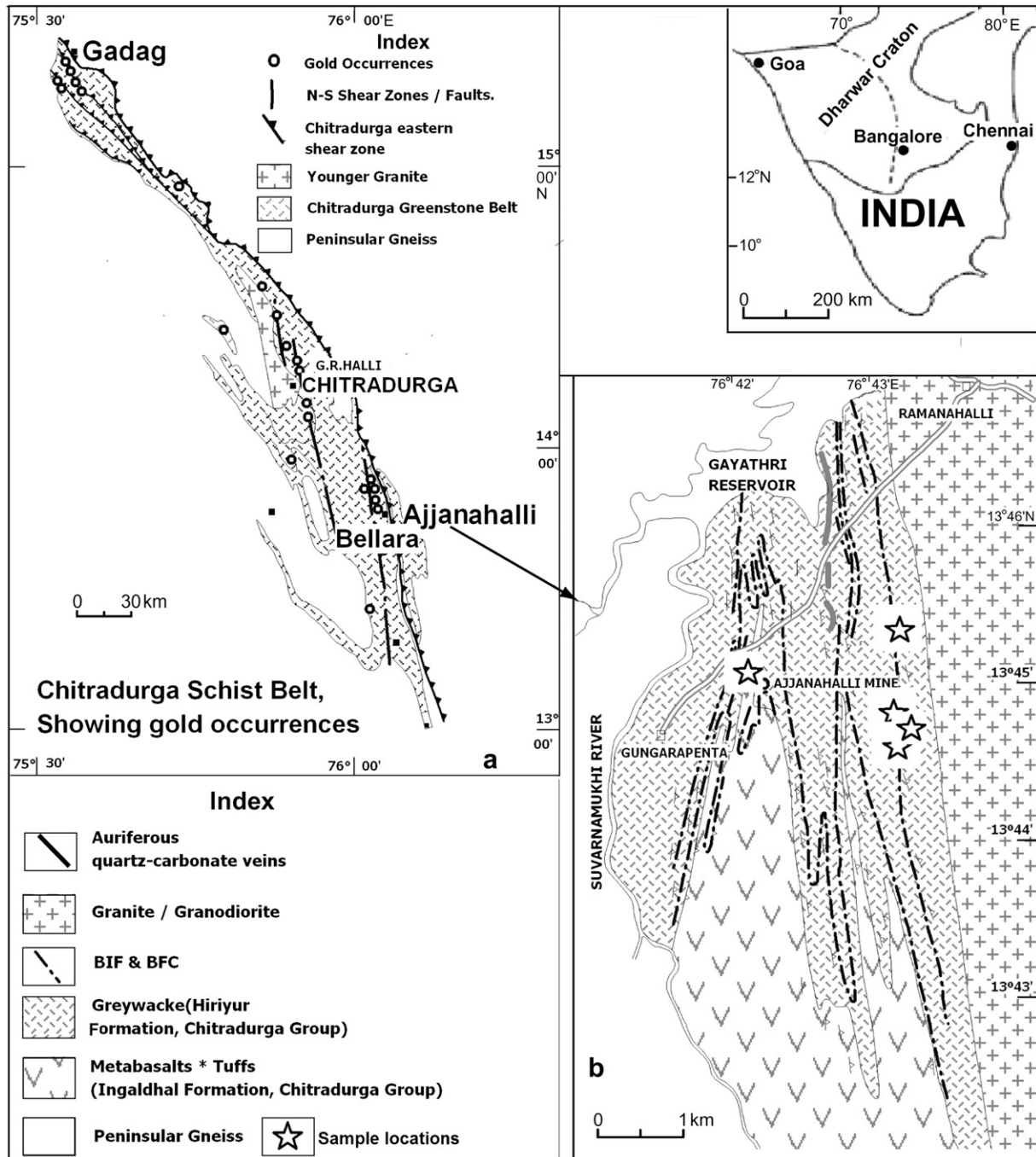


Figure 1. (a) Distribution of gold prospects of Chitradurga schist belt vis-à-vis shear zones (after Radhakrishna, 1996), (b) Geological map of Ajjanahalli gold field after Prabhakar et al. (2001) showing sample locations.

Table 1
Stratigraphic sequence of the Archean rocks of the Dharwar Craton.

Orogenic event	<2.6–2.5 Ga ^a	Orogeny with polyphase deformation, greenschist to granulite facies metamorphism, juvenile granitic magmatism, migmatization and reworking of basement, late syntectonic thrusting and sinistral strike-slip shearing	Schist belt formation from Archean sedimentary basins; granulite formation in lower crust, formation of Peninsular Gneiss by reworking of basement and migmatization of Dharwar sequence, K-feldspar granite/granodiorite emplacement including Closepet Granite and other younger granitoids
Dharwar Supergroup	2.72–2.66 Ga ^a	Chitradurga Group	Hiriyur Formations Ingaldhal Formation Vanivilas Formation
	Unconformity 2.91–2.72 Ga ^a	Bababudan Group	Quartz pebble conglomerate-quartz arenite-tholeiite-rhyodacite-carbonaceous argillite-BIF platformal to shelf association
	Non-conformity 3.4–3 Ga ^a	Basement	Gneisses and granitoids with quartzite-metapelite-carbonate-banded iron formation - Ultramafic-mafic rock inclusions

^a Geochronological informations have been taken from [Jayananda et al. \(2000\)](#) and references therein.

2. Geology of the area

2.1. Regional geological setting

The Archean Dharwar Craton of southern India ([Fig. 1](#)) has a ~3300 Ma old TTG basement complex intruded by ~3000 Ma granodiorites. Volcanic and sedimentary supracrustal rock sequence ranging in age from 2900 to 2600 Ma ([Jayananda et al., 2000](#)) constituting the well known Dharwar Supergroup non-conformably overlies this basement. The Dharwar Supergroup is intruded by 2600–2500 Ma K-feldspar rich granitoids – the Closepet Granite and its equivalents. The Neoproterozoic Dharwar Supergroup is preserved as greenstone belts or schist belts, which are the principal auriferous tracts of India ([Radhakrishna and Vaidyanathan, 2011](#)). The litho-stratigraphic sequence of the Dharwar Supergroup is given in [Table 1](#). The Dharwar Supergroup is divided into lower Bababudan Group and upper Chitradurga Group. The Bababudan Group is sub-divided into the Kalasapura, Lingadahalli and Mulaingiri Formations, and the Chitradurga Group into the Vanivilas, Ingaldhal and Hiriyur Formations ([Swami Nath and Ramakrishna, 1981](#)). The Dharwar sequence was deformed by superposed folding in a WNW-directed transpressional regime ([Chadwick et al., 1992](#)). Early isoclinal folds formed during the first phase folding were refolded coaxially during the second phase and non-coaxially along N–S axial planes during the third phase ([Naha et al., 1996](#)). During the last phase deformation, crustal scale sinistral strike-slip shear zones developed within and at the margin

of the schist belts ([Chadwick et al., 2000](#)). All the known gold occurrences in the Dharwar Craton, including the world class Kolar and Hutti gold deposits, occur within these shear zones, mainly in the Ingaldhal and Hiriyur Formations of the Chitradurga Group. The Ajjanahalli deposit occurs in such a crustal scale shear zone in the Chitradurga greenstone belt ([Fig. 1](#)).

2.2. Geological setting of Ajjanahalli gold deposit

The Ajjanahalli gold deposit is situated 80 km southeast of Chitradurga ([Fig. 1](#)). It is a small deposit with 1.75 million tonnes of gold ore reserve having an average grade of 3 g/t in the main central block. It has earlier been mined by M/S Hutti Gold Mines Ltd., by open-cast process. Quartz carbonate veins traversing the BIF carry gold mineralization which is associated with pillow basalts. The pillow lavas are devoid of vesicles or amygdales and the iron formations are carbonate and sulfide (pyrite) bearing. The non-vesicular nature of pillow lava and deposition of carbonate-sulfide iron formations suggest that they accumulated in deep water euxinic environment (cf. [Srinivasan and Naha, 1993](#)). The auriferous veins occur along N–S trending shear zones displacing the hinge zones of folds with N–S axial planes ([Prabhakar et al., 2001](#)). Gold mineralization is in the form of stringers and disseminations associated with sulfide minerals. The mineralized zone shows brecciation and wall-rock alteration including sericitization, chloritization, muscovitisation, carbonatization, etc. Gold is refractory and occurs as inclusions in pyrite and arsenopyrite.

Table 2
Summary of field and petrographic character of carbonate rocks around Ajjanahalli (based on thin section/XRD studies).

Rock units	Carbonate BIF	Carbonated metabasalt	Auriferous quartz carbonate veins (QCVs)
Outcrop	BIF is brick red colored ankerite or minor siderite and pyrite rich layers alternating with cherts layers. (Fig. 2a).	Fine grained metabasalt, pillowed and variolitic, massive, generally non-vesicular, associated with fine pyroclastic rocks-tuffs; metavolcanic rocks greenish black in color, show carbonate veins (Fig. 2c).	Milky white QCVs have traversed BIF and metabasalt. These are the main carriers of gold. The length of veins vary from 10 to 80 m (Fig. 2e). At the contact the host rocks are sericitized or muscovitised.
Texture	Fine to medium ($\geq 20 \mu\text{m}$) sparry carbonate with anhedral, deformed and elongated quartz minerals. Carbonates occur either as massive monomineralic phase laminated with alternating chert/quartzite layers (Fig. 2b).	Fine ($\sim 10 \mu\text{m}$) aggregates of actinolite, plagioclase feldspar, epidote and chlorite. Carbonate veins composed of coarse ($20\text{--}100 \mu\text{m}$) calcite (Fig. 2d)	Sparry carbonates (generally: $\leq 20\text{--}200 \mu\text{m}$, sometimes up to $800 \mu\text{m}$ or more). Quartz grains (generally $50\text{--}500 \mu\text{m}$, sometimes up to 1mm) are anhedral and deformed (Fig. 2f).
Mineralogy	Quartz, ankerite and pyrite	Actinolite, feldspar, epidote, chlorite and calcite	Quartz, calcite.

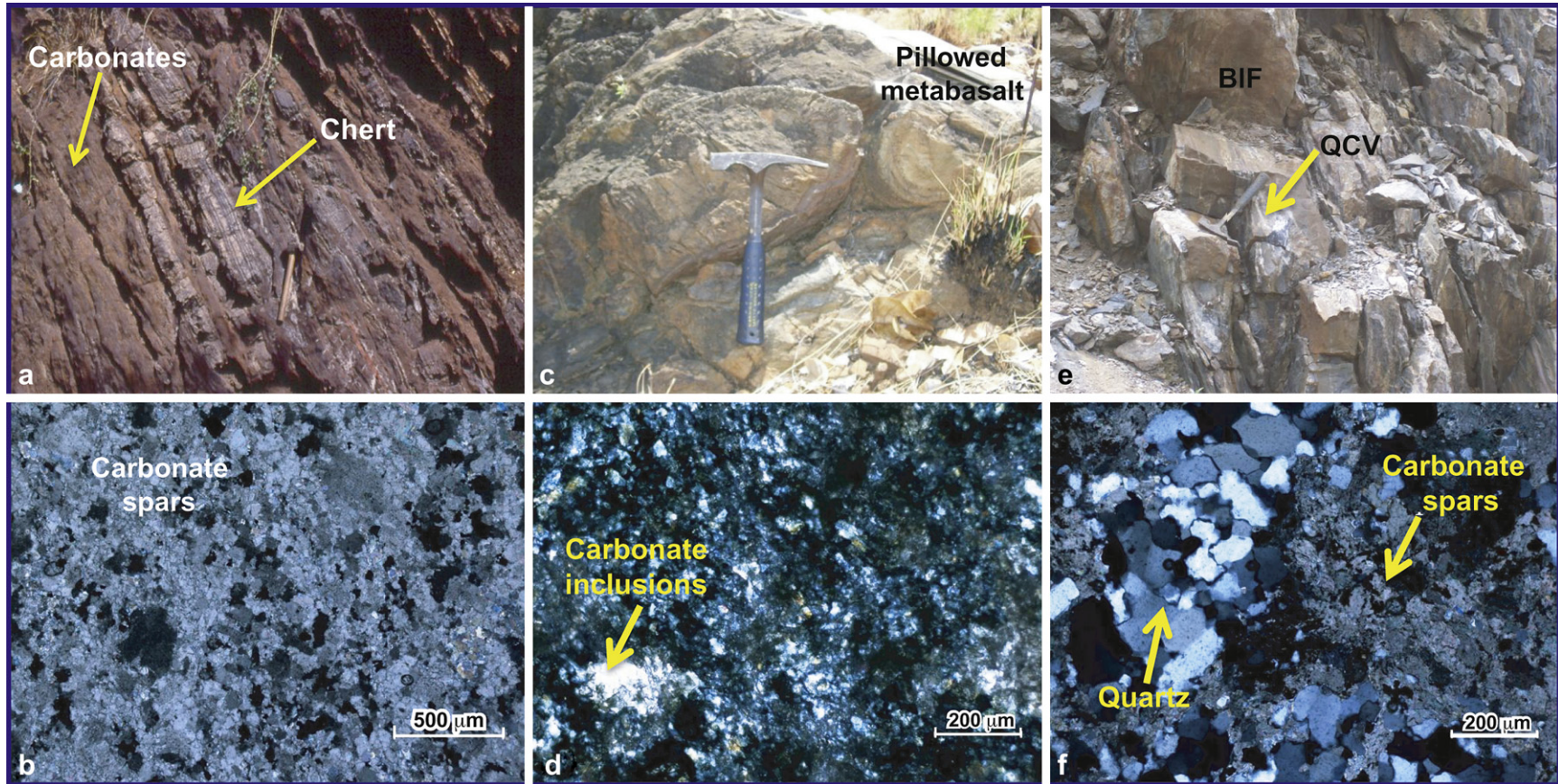


Figure 2. Field photographs of Ajjanahalli and photomicrographs of samples studied. (a) Field photograph of carbonate BIF with alternating chert layers. (b) Photomicrograph of carbonate BIF (10 \times , cross polar). (c) Field photograph of pillowed carbonated metabasalt. (d) Photomicrograph of carbonated metabasalt. (e) Field photograph of quartz carbonate veins. (f) Photomicrograph of quartz carbonate veins.

Sarma et al. (2011) have reported 2520 ± 9 Ma as the age of mineralization. Hydrothermal origin has been deduced for ore fluids based on fluid inclusion studies by Pal and Mishra (2004). Though metamorphic devolatilization of the rocks of the Chitradurga schist belt at deeper level was thought as the source of auriferous fluids (Pal and Mishra, 2004; Kolb et al., 2004), recent C and O isotope studies by Sarangi et al. (2012) have shown evidence for fluids from mantle or juvenile magmatic source. We examine REE evidence in this paper to understand better the source of the fluids and also the redox nature of the fluid at the site gold deposition.

3. Materials and methods

Samples of quartz carbonate veins (QCVs) and the host carbonate and sulfide bearing BIF were collected from the faces in the open-cast gold mine at Ajjanahalli located ~ 3.5 km WSW of Ajjanahalli village. A few samples of carbonate veins from carbonatized metabasalt, and carbonate facies BIF were also taken from

the hills located ~ 1 km SW of Ajjanahalli village for comparison. Field and petrographic characters of the carbonate rocks studied are presented in Table 2 and Fig. 2. Petrographic studies and XRD have confirmed that the carbonate of the QCVs and metabasalts is calcite and that of BIFs is ankerite (See Sarangi et al., 2012).

Carbonates were separated from the rock matrix and powdered carbonate samples from the various rock types were analyzed for REE using Inductively Coupled Plasma Mass Spectrometer (ICP-MS), model Perkin Elmer Sciex ELAN DRC II at the National Geophysical Research Institute, Hyderabad, India. Japanese Limestone (JLS-1) international reference standard was used for checking the accuracy.

4. Results

The REE data for carbonates from six quartz carbonate vein samples, five from BIF and one from metabasalt (total 12 samples) are presented in Table 3. Chondrite normalized REE patterns are shown in Fig. 3a and b.

Table 3

$\delta^{18}\text{O}(\text{‰})$, REE (ppm) and trace element (ppm) data and QCV data of carbonates from auriferous quartz carbonate veins and associated rocks and carbonate BIFs of the Ajjanahalli. $\delta^{18}\text{O}$ and mineral phases are based on XRD study (after Sarangi et al., 2012).

$\delta^{18}\text{O}(\text{‰})$, REE (ppm) and trace element (ppm) data of QCVs of Ajjanahalli						
Element	AJ-16(W)	AJ-16(IV)	AJ-16(WR)-2	AJ-16(V)2-hst	AJ-16(V)2-vn	AJ-16
$\delta^{18}\text{O}(\text{‰})$	16.94	23.80	18.56	11.41	11.49	13.60
La	3.56	5.70	6.29	8.94	8.23	3.66
Ce	4.10	8.46	10.75	13.94	12.62	4.20
Pr	0.49	1.07	1.48	1.82	1.56	0.48
Nd	1.86	4.46	6.34	7.58	6.36	1.83
Sm	0.36	1.13	2.04	1.86	1.63	0.37
Eu	0.28	0.61	1.11	0.87	0.84	0.29
Gd	0.52	1.47	2.31	2.18	2.04	0.54
Tb	0.12	0.30	0.60	0.48	0.47	0.12
Dy	0.90	1.70	3.70	2.97	3.13	0.89
Ho	0.26	0.38	0.82	0.62	0.66	0.26
Er	0.83	0.97	2.45	1.64	1.77	0.81
Tm	0.15	0.16	0.45	0.27	0.30	0.15
Yb	0.92	0.88	3.06	1.70	1.78	0.90
Lu	0.16	0.15	0.57	0.27	0.27	0.16
Sr	135.99	303.04	610.11	327.06	767.33	136.31
Ba	16.80	12.09	15.88	12.71	9.85	17.38
Zr	3.39	3.74	8.07	26.20	2.87	3.17
ΣREE	14.50	27.45	41.99	45.15	41.66	14.65
ΣLREE	10.37	20.82	26.90	34.14	30.41	10.53
ΣHREE	4.13	6.63	15.09	11.01	11.25	7.16
$(\text{La}/\text{Lu})_{\text{N}}$	2.25	3.87	1.14	3.46	3.15	2.41
$(\text{La}/\text{Yb})_{\text{N}}$	2.62	4.37	1.39	3.56	3.13	2.75
Eu/Eu^*	1.96	1.45	1.56	1.32	1.41	1.98
Mineral phases	Q + Cc		Cc + Q + CcL	Q + Cc + Ank		
REE (ppm) and trace element (ppm) data of carbonate BIFs and metabasalt of Ajjanahalli						
Element (ppm)	AJ-13	AJ-6	AJ-14	AJ-9	AJ-5 (metabasalt)	
La	1.93	2.40	1.63	1.51	5.33	
Ce	2.61	3.29	2.16	2.26	13.09	
Pr	0.36	0.43	0.26	0.28	2.17	
Nd	1.33	1.58	1.00	1.02	10.89	
Sm	0.28	0.38	0.22	0.20	3.55	
Eu	0.17	0.25	0.16	0.13	1.25	
Gd	0.37	0.42	0.29	0.27	3.91	
Tb	0.09	0.10	0.06	0.07	0.97	
Dy	0.52	0.64	0.41	0.40	6.46	
Ho	0.14	0.16	0.11	0.11	1.39	
Er	0.42	0.48	0.33	0.30	3.74	
Tm	0.08	0.09	0.07	0.06	0.66	
Yb	0.42	0.61	0.33	0.32	3.70	
ΣREE	8.79	10.94	7.06	6.98	57.64	
$(\text{La}/\text{Lu})_{\text{N}}$	2.50	2.17	2.73	2.79	1.06	
$(\text{La}/\text{Yb})_{\text{N}}$	3.07	2.64	3.38	3.16	0.97	
Eu/Eu^*	1.66	1.88	1.90	1.75	1.02	
Mineral phases	Ank					

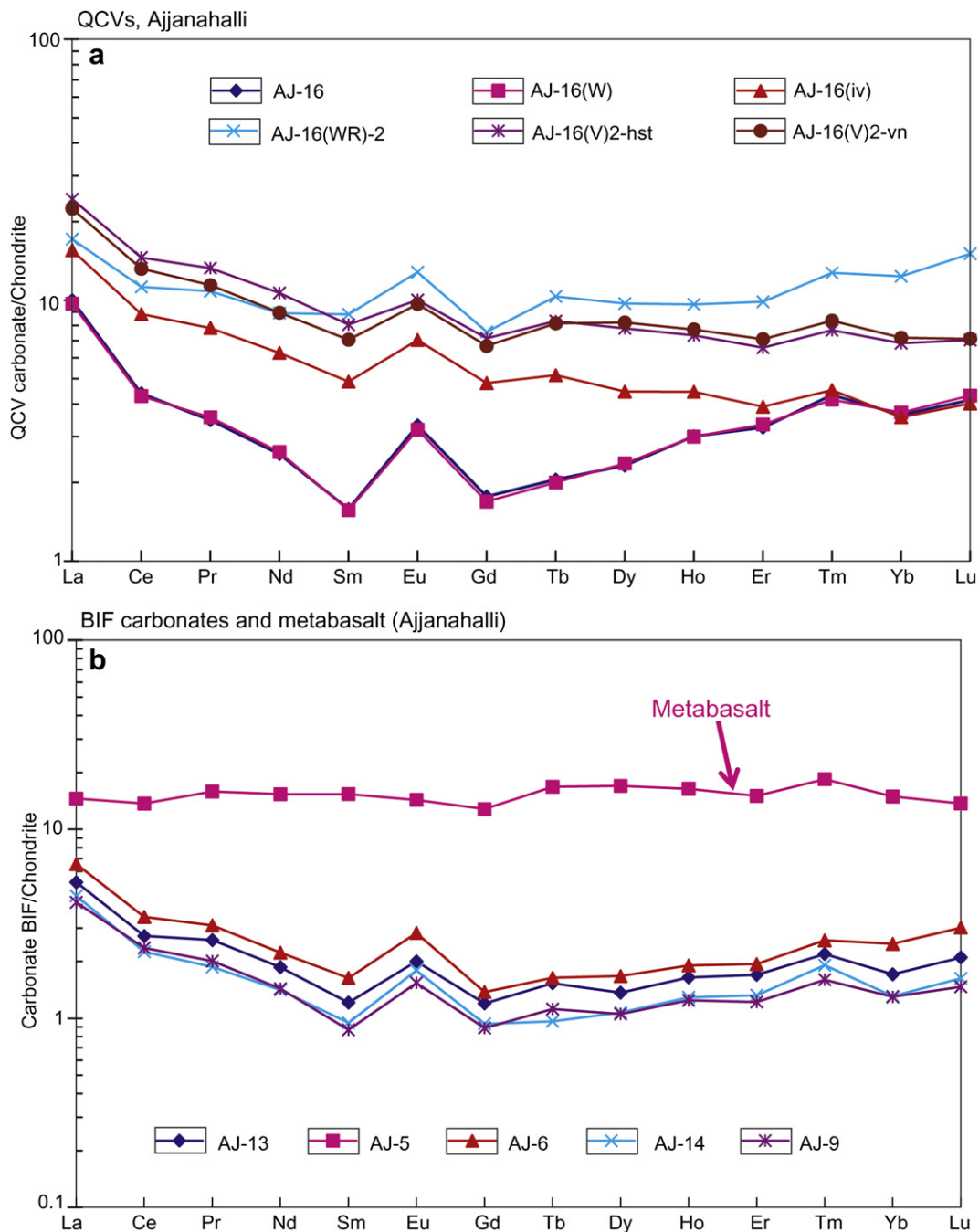


Figure 3. (a) Chondrite normalized REE plots of QCVs of Ajjanahalli, and (b) Chondrite normalized REE plots of carbonate BIFs and metabasalt of Ajjanahalli.

4.1. REE of carbonates of QCV

The Σ REE values of QCV carbonates range between 14.5 and 45.14 ppm (average 30.9 ± 14.05). Although, there is a mild enrichment of LREE over HREE with $(La/Yb)_N$ ranging between 2.62 and 4.37 (average 2.97 ± 1.00) and $(La/Lu)_N$ ranging from 1.14 to 3.87 (average 2.71 ± 0.98). Chondrite normalized REE plots (Fig. 3a) clearly show concave upward U-shaped REE pattern with enrichment of both LREE and HREE. A distinct positive Eu anomaly (Eu/Eu^*) in the range of 1.32–1.98, average 1.61 ± 0.3 is observed.

4.2. REE of carbonates of BIF

The Σ REE of BIF carbonates range from 6.98 to 10.94 ppm (average 8.44 ± 1.86 ppm). The chondrite normalized REE plot (Fig. 3b) shows LREE enriched and flat HREE pattern with a positive Eu anomaly (Eu/Eu^* range: 1.01–1.90; average: 1.8 ± 0.1). Slight enrichment of LREE over HREE is reflected also by from $(La/Lu)_N$ values ranging between 1.06 and 2.79 (average: 2.55 ± 0.3) and $(La/Yb)_N$ ranging between 2.64 and 3.38 (average 3.06 ± 0.3). In respect of having low abundance of Σ REE and positive Eu anomaly, the iron formations resemble the Archean sedimentary formations

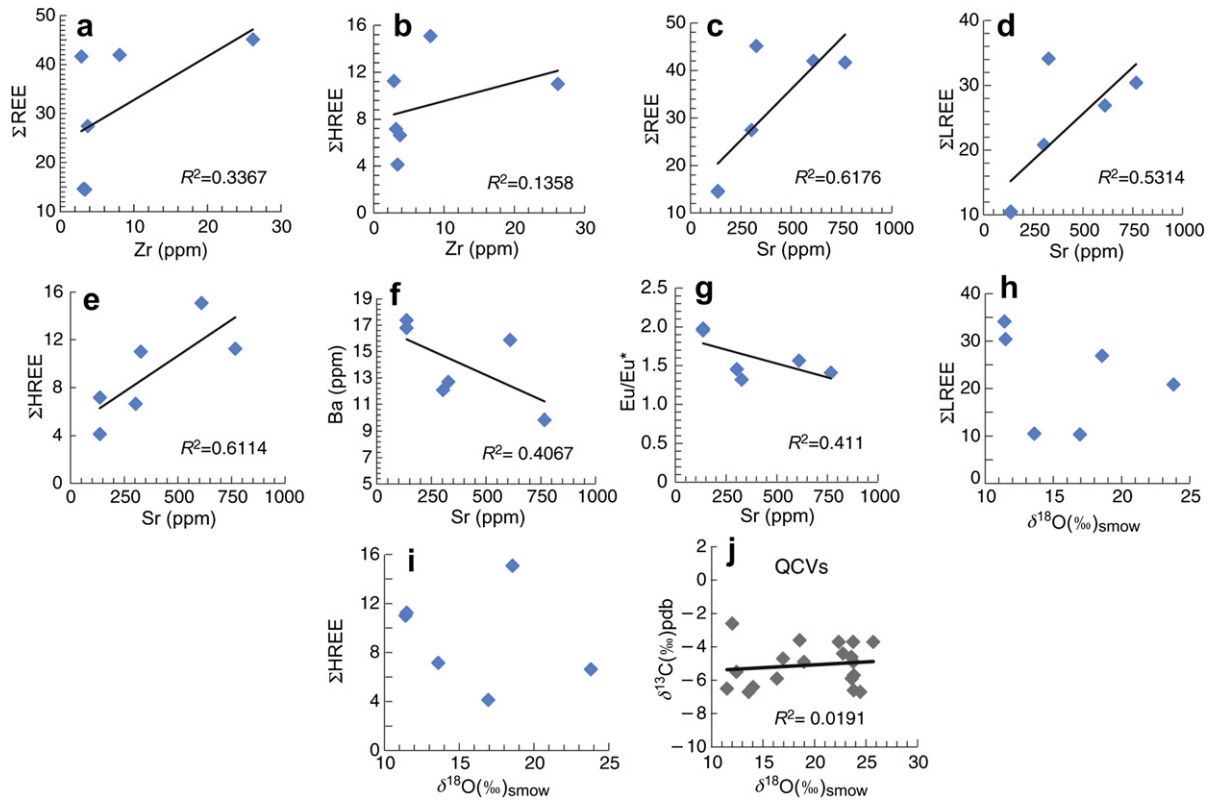


Figure 4. Correlation diagrams (a) Zr-ΣREE, (b) Zr-ΣHREE, (c) Sr-ΣREE, (d) Sr-ΣLREE, (e) Sr-ΣHREE, (f) Sr-Ba, (g) Sr-Eu/Eu*, (h) $\delta^{18}\text{O}$ -ΣLREE, (i) $\delta^{18}\text{O}$ -ΣHREE, (j) plot of $\delta^{18}\text{O}$ (smow) vs $\delta^{13}\text{C}$ (pdb) for the carbonates of Ajjanahalli (Data taken from Sarangi et al., 2012) from mineralized quartz carbonate veins.

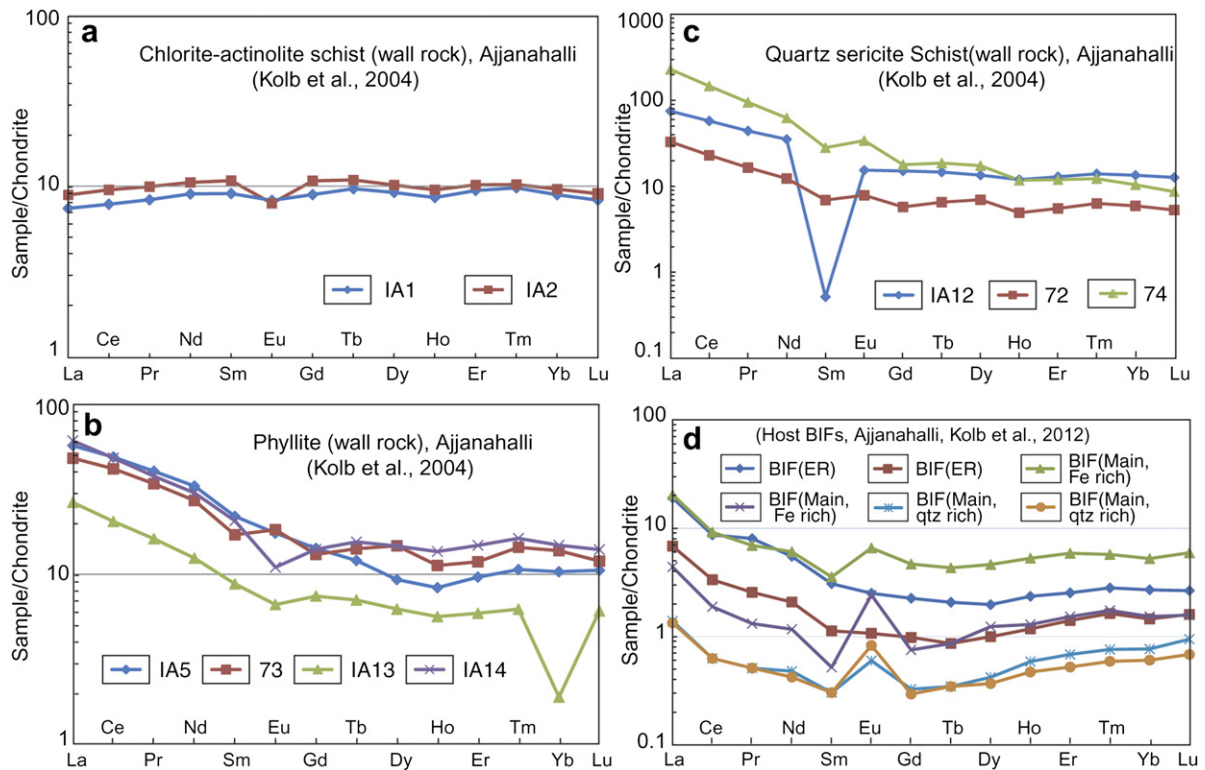


Figure 5. Chondrite normalized REE plot of different wall rocks after Kolb et al. (2004). (a) Chlorite-actinolite schist; (b) Phyllites; (c) Quartz-sericite schist; (d) Host BIFs.

deposited in reducing waters (cf. Chen and Zhao, 1997; Tang et al., in press).

4.3. REE of carbonates in metabasalt

The Σ REE of the carbonates of metabasalt is of the order 57.64 ppm and is much higher than that in carbonates of QCV or BIF. Chondrite normalized REE plot of carbonate from metabasalt shows flat REE pattern without any significant enrichment of LREE over HREE ((La/Lu)_N: 1.06; (La/Yb)_N: 0.97). Also no significant Eu anomaly is observed (Eu/Eu* range: 1.02) (Fig. 3b).

5. Discussion

In the following discussion we critically evaluate the reasons for the observed REE patterns of the auriferous QCVs which show characteristic positive Eu anomaly. Kontak and Jackson (1999) proposed that such REE patterns could be due to one of the following reasons:

- (i) Presence of micro-inclusions of minerals such as zircon, scheelite, monazite, xenotime;
- (ii) Contamination from wall rocks;
- (iii) Presence of Eu rich feldspar;
- (iv) Post-depositional alteration;
- (v) Inherent nature of the fluid from the source with appropriate temperature, pH and oxidation (i.e. $f(\text{O}_2)$) condition of the fluid.

Petrographic studies of the analyzed QCVs do not show the presence of mineral phases such as zircon, monazite, apatite, xenotime or scheelite in them. X-ray diffraction data corroborate this inference. However, it may be stated that XRD cannot detect any mineral whose abundance is less than 5%, Σ REE values of QCVs are very low. Presence of one or more of the above mineral phases would have resulted in higher abundances of REE which is not the case. Also, there is no correlation between Zr- Σ REE (Fig. 4a) and Zr- Σ HREE in binary plots (Fig. 4b). In the light of the foregoing discussion, we infer that the REE abundances and patterns of the QCV carbonates cannot be due to the contribution of REE rich mineral phases such as zircon or monazite etc.

There is a poor positive correlation between Sr- Σ REE (Fig. 4c), Sr- Σ LREE (Fig. 4d), Sr- Σ HREE (Fig. 4e) and negative correlation between Sr-Ba (Fig. 4f), and Sr-Eu/Eu* (Fig. 4g). These relationships preclude plagioclase as a contributing mineral to the REE abundance or Eu/Eu* anomaly.

In the metamorphic devolatilization model for the orogenic gold deposits, the auriferous fluid is considered to be derived from the breakdown of hydrous and carbonate minerals during progressive metamorphism (Kerrick and Fyfe, 1981). Comparison of REE patterns of QCVs with those of associated rocks (Fig. 5, Kolb et al., 2004) shows that REE patterns of QCVs in respect of having slight LREE enrichment and positive Eu anomaly are some what similar only to that of host BIF. However, the total REE of the former are much higher than the latter. If fluids for QCVs were derived from BIF during metamorphism, mass balance considerations require that the REE pattern for the carbonates of QCVs and BIFs should be complementary. But the REE pattern of QCVs is not complementary to those of the BIFs.

The QCV carbonates are characterized by a wide range of $\delta^{18}\text{O}$ values from a very low 11.41‰ to values as heavy as 23.8‰. The cross plot $\delta^{13}\text{C}/\delta^{18}\text{O}$ for the QCV carbonates is given in Fig. 4j after Sarangi et al. (2012). It is obvious that there is no correlation ($R^2 = 0.02$) between the two. However, a trend nearly parallel to $\delta^{18}\text{O}$ axis is observed. This may be due to partial resetting of $\delta^{18}\text{O}$

caused by alteration by fluids with lower fluid/rock ratio as exemplified by Tang et al. (2011, in press) and Guerrero et al. (1997). It is however pertinent to note that such heavy $\delta^{18}\text{O}$ (up to 23.8‰) is also found in many altered igneous carbonates like in carbonatite, which have been affected by meteoric water alteration at very low temperature (Le Bass, 1999; Gwalani et al., 2010).

Use of REEs for genetic interpretations relies largely upon the fact that these elements are generally immobile (Barth et al., 1993; Cousens et al., 1993) although there are exceptions (Wendlandt and Harrison, 1979; Rolland et al., 2003). But such mobilization only takes place at a very high water-rock ratio (Bau, 1993). Though a partial resetting of $\delta^{18}\text{O}$ cannot be ruled out, lack of correlation between $\delta^{18}\text{O}$ and LREE (Fig. 4h) and $\delta^{18}\text{O}$ and HREE (Fig. 4i) signifies no effect of low temperature alteration on REEs. Based on the discussion presented above, we consider the REE patterns of QCVs as pristine signature and could reflect inherent nature of the fluid from the source.

QCVs with strong positive Eu anomaly have been reported in auriferous quartz veins of Sovetskoye orogenic gold deposits, Russia (Tomilenko et al., 2008, 2010) which has been attributed to migration of reducing gold bearing fluids enriched in Eu^{2+} along faults zones from lower part of continental crust or mantle to the sites of ore deposition (Taylor and McLennan, 1985). Raman Spectroscopic analysis of fluid inclusions in quartz of this deposit has revealed highly reduced fluid systems in auriferous zones with $\text{CO}_2/\text{CH}_4 \leq 22$. Similar scenario holds good for the Ajjanahalli gold deposits. The deposit is located on a 400 km long crustal scale shear zone known as Chitradurga Boundary Shear Zone (Kolb et al., 2004). Such crustal scale shear zones have been proposed to penetrate very deep to tap CO_2 rich fluids from mantle (Pili et al., 1997). The $\delta^{13}\text{C}$ composition of the QCV carbonates ($-5.5 \pm 1.3\text{‰}$), and calculated fluid $\delta^{13}\text{C}$ ($-5.81 \pm 1.14\text{‰}$) reported by Sarangi et al. (2012) is in favor of mantle source of the fluids for the Ajjanahalli deposit. Narrow range of $\delta^{34}\text{S}$ ($2.1\text{--}2.7\text{‰}$; Kolb et al., 2004 and $3.3\text{--}4.6\text{‰}$; Sarvanan and Mishra, 2009) of Au-bearing sulfides of this deposit also indicate mantle/magmatic sulfur. Pal and Mishra (2004) have reported CO_2/CH_4 ratio of 7.13 for the fluids by Raman Spectroscopic study of fluid inclusions of this deposit. This indicates highly reduced nature of the ore fluid.

Positive Eu anomaly arises from low oxygen fugacity condition of the fluid (Drake and Weill, 1975; Bau, 1993; Chen and Zhao, 1997). Chen and Zhao (1997) have suggested that when $f(\text{O}_2)$ is low the anions will be prevailed by soft bases such as HS^- , S^{2-} , SCN^- , $\text{S}_2\text{O}_3^{2-}$, CO , CH_4 , and low values of $\text{Eu}^{3+}/\text{Eu}^{2+}$. Eu is dominated by Eu^{2+} . As a kind of acid, Eu^{2+} is softer than trivalent REE ions (R^{3+}) including Eu^{2+} which are all hard acids. Eu^{2+} is easier than R^{3+} to combine with soft bases into stable complexes and to precipitate from water thereby generating +ve Eu anomaly. Hence the positive Eu anomaly of carbonates of QCVs indicates that auriferous fluids were characterized by low oxygen fugacity which is also supported by reduced nature of the fluid ($\text{CO}_2/\text{CH}_4 = 7.13$, Pal and Mishra, 2004).

According to Cameron and Hattori (1987) such fluids give rise to smaller gold deposits compared to the fluids that are characterized by high oxygen fugacity fluids which produce world class deposits. The small tonnage of gold deposits of Ajjanahalli in the Dharwar Craton supports this inference.

6. Conclusion

REE evidence is in favor of the formation of auriferous quartz veins from reducing fluids derived from mantle source and channeled through crustal scale shear zone traceable along the eastern margin of the Chitradurga schist belt in the Dharwar Craton. The strong positive Eu anomaly shown by QCV carbonates serves as evidence for low oxygen fugacity (reduced nature) of the fluid.

Acknowledgment

The work was initiated by SS when he was a geologist in GSI, Bangalore followed by funding through Minor Research Project from Indian School of Mines, Dhanbad and SERC, Department of Science & Technology, New Delhi, India.

References

- Barth, S., Oberli, F., Meier, M., Blattner, P., Bargossi, G.M., DiBattistini, G., 1993. The evolution of a calc-alkaline basic to silicic magma system: geochemical and Rb-Sr, Sm-Nd, and $^{18}\text{O}/^{16}\text{O}$ isotopic evidence from the Late Hercynian Atesina-Cima d'Asta volcano-plutonic complex, Northern Italy. *Geochimica et Cosmochimica Acta* 57, 4285–4300.
- Bau, M., 1993. Rare-earth element mobility during hydrothermal and metamorphic fluid-rock interaction and the significance of the oxidation state. *Chemical Geology* 93, 219–230.
- Burrows, D.R., Wood, P.C., Spooner, E.T.C., 1986. Carbon isotope evidence for a magmatic origin for Archaean gold quartz vein ore deposits. *Nature* 321, 851–854.
- Cameron, E.M., Hattori, K., 1987. Archaean gold mineralization and oxidized hydrothermal fluids. *Economic Geology* 82, 1177–1191.
- Chadwick, B., Vasudev, V.N., Krishna, Rao, Hegde, G.V., 1992. The Dharwar supergroup: basin development and implications for Late Archaean tectonic setting in western Karnataka, southern India. In: Glover, J.E., Ho, S. (Eds.), *The Archaean: Terrains, Processes and Metallogeny*. University of Western Australia, pp. 3–15. Publication 22.
- Chadwick, B., Vasudev, V.N., Hedge, G.V., 2000. The Dharwar craton, southern India, interpreted as the result of Late Archaean oblique convergence. *Precambrian Research* 99, 91–111.
- Chen, Y.J., Zhao, Y.C., 1997. Geochemical characteristics and evolution of REE in the Early Precambrian sediments: evidences from the southern margin of the North China Craton. *Episodes* 20, 109–116.
- Cousens, B.L., Spera, F.J., Dobson, P.F., 1993. Post-eruptive alteration of silicic ignimbrites and lavas, Gran Canaria, Canary Islands: strontium, neodymium, lead and oxygen isotopic evidence. *Geochimica et Cosmochimica Acta* 57, 631–640.
- Drake, M.J., Weill, D.F., 1975. Partition of Sr, Ba, Ca, Y, Eu^{2+} , Eu^{3+} , and other REE between plagioclase feldspar and magmatic liquid: an experimental study. *Geochimica et Cosmochimica Acta* 39, 689–712.
- Goldfarb, R.J., Baker, T., Dube, B., Groves, D.I., Hart, C.J.R., Gosselin, P., 2005. Distribution, Character and Genesis of Gold Deposits in Metamorphic Terranes. In: *Economic Geology 100th Anniversary Volume*, pp. 407–450.
- Groves, D.I., Goldfarb, R.J., Robert, F., Hart, C.J.R., 2003. Gold deposits in metamorphic belts: overview of current understanding, outstanding problems, future research, and exploration significance. *Economic Geology* 98, 1–29.
- Groves, D.I., Golding, S.D., Rock, N.M.S., Barley, M.E., McNaughton, N.J., 1988. Archaean carbon reservoirs and their relevance to the fluid source for gold deposits. *Nature* 321, 254–257.
- Guerrera, A., Peacock, S.M., Knauth, L.P., 1997. Large ^{18}O and ^{13}C depletion in greenschist facies carbonate rocks, western Arizona. *Geology* 25, 943–946.
- Gwalani, L.G., Rogers, K.A., Demény, A., Groves, D.I., Ramsay, R., Beard, A., Downes, P.J., Eves, A., 2010. The Yungul carbonatite dykes associated with the epithermal fluorite deposit at Speewah, Kimberley, Australia: carbon and oxygen isotope constraints on their origin. *Mineralogy and Petrology* 98, 123–141.
- Jayananda, M., Moyen, J.F., Martin, H., Peucat, J.J., Auvray, B., Mahabaleswar, B., 2000. Late Archaean (2550–2520 Ma) juvenile magmatism in the Eastern Dharwar craton, southern India: constraints from geochronology, Nd–Sr isotopes and whole rock geochemistry. *Precambrian Research* 99, 225–254.
- Kerrich, R., 1983. *Geochemistry of Gold Deposits in Abitibi Greenstone Belt*. Special paper. 27. Canadian Institute of Mining and Metallurgy, Ontario, Canada, 75 pp.
- Kerrich, R., Fyfe, W.S., 1981. The gold carbonate association: source of CO_2 and CO_2 -fixation reactions in Archaean lode deposits. *Chemical Geology* 33, 265–293.
- Kolb, J., Hellmann, A., Rogers, A., Sindern, S., Venneman, T., Botcher, M.E., Meyer, F., 2004. The role of a transcrustal shear zone in orogenic gold mineralization at the Ajjanahalli Mine, Dharwar Craton, South India. *Economic Geology* 99, 743–759.
- Kontak, D.J., Jackson, S.J., 1999. Documentation of variable trace and rare earth element abundances in carbonates from auriferous quartz veins in Maguma lode gold deposits, Nova Scotia. *The Canadian Mineralogist* 37, 469–488.
- Le Bass, M.J., 1999. Ferrocarnatites: geochemistry and magma-fluid state. *Memoir Geological Society of India* 43, 785–802.
- McCuaig, T.C., Kerrich, R., 1998. P-T-t-deformation-fluid characteristics of lode gold deposits: evidence from alteration systematic. *Ore Geology Reviews* 12, 381–453.
- Mikucki, E.J., Ridley, J.R., 1993. The hydrothermal fluid of Archaean lode gold deposits at different metamorphic grades: compositional constraints from ore and wall rock alteration assemblages. *Mineralium Deposita* 28, 469–481.
- Naha, K., Srinivasan, R., Mukhopadhyay, D., 1996. Structural studies and their bearing on Early Precambrian history of Dharwar tectonic province, southern India. *Proceedings of the Indian Academy of Sciences (Earth and Planetary Sciences)* 105, 379–412.
- Nesbitt, B.E., 1988. The gold deposit continuum: a genetic model for lode Au-mineralization in the continental crust. *Geology* 15, 1044–1048.
- Pal, N., Mishra, B.M., 2004. Epigenetic nature of BIF-hosted gold mineralization at Ajjanahalli, southern India: evidence from ore petrography and fluid inclusion studies. *Gondwana Research* 6, 531–540.
- Pili, É., Ricard, Y., Lardeaux, J.M., Sheppard, S.M.F., 1997. Lithospheric shear zones and mantle-crust connections. *Tectonophysics* 280, 15–29.
- Prabhakar, K.N., Nagaraja Rao, K.N., Ramachandra, N.D., 2001. BIF-hosted epigenetic gold mineralization and exploration in Ajjanahalli area, Tumkur district, Karnataka. *Geological Survey of India Special Publication* 58, 279–287.
- Radhakrishna, B.P., 1996. Mineral resources of Karnataka. *Geological Society of India, Mineral Resources of India* 8, 214–279.
- Radhakrishna, B.P., Vaidyanathan, R., 2011. *Geology of Karnataka*. Geological Society of India, 353p.
- Ridley, J.R., Diamond, L.W., 2000. Fluid chemistry of orogenic lode gold deposits and implications for genetic models. *Society Economic Geology Reviews* 13, 141–162.
- Rock, N.M.S., Groves, D.I., Perring, C.S., Golding, S.D., 1989. Gold, lamprophyres and porphyries: what does their association mean? *Economic Geology Monograph* 6, 609–625.
- Rolland, Y., Cox, S., Boullier, A.M., Pennacchioni, G., Mancktelow, N., 2003. Rare earth and trace element mobility in mid-crustal shear zones: insights from the Mont Blanc Massif (Western Alps). *Earth and Planetary Science Letters* 214, 203–219.
- Santosh, M., 1992. Role of mantle carbon in Archaean gold genesis in South India: evidence from carbon stable isotopic composition of fluid inclusions. *Journal Geological Society of India* 40, 127–134.
- Sarangi, S., Sarkar, A., Srinivasan, R., Patel, S.C., 2012. Carbon isotope studies of auriferous quartz carbonate veins from two orogenic gold deposits from the Neoproterozoic Chitradurga schist belt, Dharwar craton, India: evidence for mantle/magmatic source of auriferous fluid. *Journal of Asian Earth Sciences* 52, 1–11.
- Sarma, D.S., Fletcher, I.R., Rasmussen, B., McNaughton, N.J., Ram Mohan, M., Groves, D.I., 2011. Archaean gold mineralisation of the Western Dharwar Craton, India: 2.52 Ga U–Pb ages of hydrothermal monazite and xenotime in gold deposits. *Mineralium Deposita* 46, 273–288.
- Sarvanan, C., Mishra, B.M., 2009. Uniformity in sulphur isotope composition in the orogenic gold deposits from the Dharwar Craton, southern India. *Mineralium Deposita* 44, 597–605.
- Srinivasan, R., Naha, K., 1993. Archean sedimentation in the Dharwar craton, southern India. *Proceedings of National Academy of Sciences Of India* 63, 1–13.
- Swami Nath, J., Ramakrishna, M., 1981. Early precambrian supracrustals of Karnataka. *Memoirs of the Geological Survey of India* 112, 328.
- Tang, H., Chen, Y., Santosh, M., Zhong, H., Yang, T. REE geochemistry of carbonates from the Guanmenshan Formation, Liaoh Group, NE Sino-Korean Craton: implications for seawater compositional change during the Great Oxidation Event. *Precambrian Research*, in press.
- Tang, H.S., Chen, Y.J., Wu, G., Lai, Y., 2011. Paleoproterozoic positive $\delta^{13}\text{C}_{\text{carb}}$ excursion in northeastern Sino-Korean Craton: evidence of the Lomagundi Event. *Gondwana Research* 19, 471–481.
- Taylor, S.R., McLennan, S.M., 1985. *The Continental Crust: Its Composition and Evolution: An Example of the Geochemical Record Preserved in Sedimentary Rocks*. Blackwell, Oxford, 312 pp.
- Tomilenko, A., Gibsher, N., Dublyansky, Y., Dallai, L., 2010. Geochemical and isotopic properties of fluids from gold-bearing and barren quartz veins of the Sovetskoye gold deposits (Siberia, Russia). *Economic Geology* 105, 375–394.
- Tomilenko, A., Gibsher, N.A., Kozmenko, O.A., Palesskii, S.V., Nikolaeva, I.V., 2008. Lanthanides in fluid inclusions, quartz and greenschists from auriferous and barren quartz vein zones of the Sovetskoye quartz-gold deposit. *Geochemistry International* 46, 402–408.
- Wendlandt, R.F., Harrison, W.J., 1979. Rare earth partitioning between immiscible carbonate and silicate liquids and CO_2 vapour: results and implications for the formation of light rare-earth-enriched rocks. *Contributions to Mineralogy and Petrology* 69, 409–419.