Granite-hosted molybdenite mineralization from Archean Bundelkhand craton-molybdenite characterization, host rock mineralogy, petrology, and fluid inclusion characteristics of Mo-bearing quartz

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The dominantly high-K, moderate to high SiO₂ containing, variably fractionated, volcanic-arc granitoids ($\pm$ sheared) from parts of Bundelkhand craton, northcentral India are observed to contain molybdenite (Mo) in widely separated 23 locations in the form of specks, pockets, clots and stringers along with quartz $\pm$ pyrite $\pm$ arsenopyrite $\pm$ chalcopyrite $\pm$ bornite $\pm$ covellite $\pm$ galena $\pm$ sphalerite and in invisible form as well. The molybdenite mineralization is predominantly associated with Bundelkhand Tectonic Zone, Raksa Shear Zone, and localized shear zones. The incidence of molybdenite is also observed within sheared quartz and tonalite–trondhjemite–granodiorite (TTG) gneisses. The fluid inclusion data show the presence of bi-phase (H₂O–CO₂), hypersaline and moderate temperature (100°–300°C) primary stretched fluid inclusions suggesting a possible hydrothermal origin for the Mo-bearing quartz occurring within variably deformed different granitoids variants of Archean Bundelkhand craton.

1. Introduction

The Archean Bundelkhand craton (hereinafter referred to as ABC) is one of the five Archean cratons (Aravalli, Bastar, Bundelkhand, Dharwar, and Singhbhum) exposed in the peninsular shield that occupies an area of $\sim 29,000$ km² in north-central India (figure 1). It is the least known for its granite-hosted mineral resources except for pyrophyllite and diaspore (Sharma 1979), gold mineralization (Pati *et al.* 1997) and recently discovered uranium content (Pathak *et al.* 2009) in the impact melt breccias of granitic composition from Dhala structure (Pati *et al.* 2008a). The incidences of molybdenite mineralization have been reported based on preliminary findings from the ABC (Shukla and Singh 1997; Nim and

Hasan 1997; Pati 1997; Pati and Panigrahi 2005). However, studies on molybdenite associated with copper-gold of Late Archean–Early Proterozoic age are very well known from Malanjkhand, Madhya Pradesh state, India (Panigrahi *et al.* 1993; Panigrahi and Mookherjee 1997; Stein *et al.* 2004; Pandit and Panigrahi 2012) from the adjacent Bastar craton. Molybdenite associated mineral deposits from India and other parts of the world are known to be good indicators of geodynamic settings (Sillitoe 1972; Panigrahi and Mookherjee 1997; Corbett and Leach 1998; Santosh 1999; Richards 2003; Hou *et al.* 2009) and molybdenite is extensively used to date the mineralization event (Santosh 1988a, b; Mao *et al.* 1999; Stein *et al.* 1997, 2004; Stein 2006;

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Figure 1. A simplified map of Bundelkhand craton showing regional geology, locations of Mo-bearing rocks (solid dots), Au incidences (solid triangles; after Pati *et al.* 1997), Raksa Shear Zone (RSZ) and Bundelkhand Tectonic Zone (BTZ).

Li *et al.* 2011; Delibaş and Genç 2012). Here, we present a detailed report on molybdenite mineralization from parts of the ABC with host

rock mineralogy and petrology and the first fluid inclusion data from Mo-bearing quartz from granitoids.

2. Geology and geochronology of Archean Bundelkhand craton (ABC)

The ABC comprises mainly granitoids (including TTG; Sharma and Rahman 1995). The meta-supracrustal rocks comprise banded iron formations (BIF), ultra high pressure (UHP) corundum-bearing phengite schist (Saha *et al.* 2010), inter-bedded quartzites, calc-silicate gneisses, metamorphosed ultramafic rocks of komatiitic affinity (similar to modern boninites; Malviya *et al.* 2006), amphibolites, metamorphosed pillow lavas, and volcanoclastic metasediments. These metasupracrustal slivers occurring in variably deformed granitoids are inferred to be the remnants of supra-subduction crust tectonically emplaced during Archean arc-continent-continent collision (Malviya *et al.* 2006). The temporally distinct tectonically controlled multiple phases of silicothermal fluid activity resulting in NNE–SSW to NE–SW trending quartz veins within granitoids and supracrustals are the most conspicuous linear to curvilinear features observed in the ABC (Pati *et al.* 2007). These veins are in turn intruded by NW–SE trending mafic dykes of tholeiitic affinity (Pati *et al.* 2008b). The pink to grey coloured, porphyritic granitoids in the ABC include syeno- and monzogranite, granodiorite, diorite, alkali feldspar syenite, granite porphyry and rhyolite (Sarkar *et al.* 1984; Rahaman and Zainuddin 1993; Mondal *et al.* 2002; Pati *et al.* 2007, 2008a, b). They are typically metaluminous–peraluminous, alkaline to calc-alkaline, volcanic-arc granitoids and show LREE-enriched and HREE-depleted pattern with a negative Eu anomaly.

The metamorphic evolution of the Bundelkhand craton is poorly constrained. Basu (1986) reported greenschist to amphibolite facies metamorphism for the basement gneisses and schists, whereas Saha *et al.* (2010) reported eclogite facies condition with peak P–T of 20 kbar and 650°C for margarite–phengitic muscovite–chlorite corona mantled corundum-bearing quartz-free high-Mg, Al phlogopite–chlorite schists intruded by 3.2–3.4 Ga old TTG.

The Pb–Pb isochron ages of zircons determined by Ion Probe and SHRIMP techniques from some of the Bundelkhand granitoids range from 2492 to 2551 Ma in rhyolite/granophyre/granite porphyry and 2563 ± 6 Ma in diorite (Mondal *et al.* 2002; Pati *et al.* 2010) and are suggested to be the stabilization age of the craton (Mondal *et al.* 2002). Pati *et al.* (2010) have dated the zircons from the granitoids from NW parts of Bundelkhand craton by SHRIMP dating techniques and reported ages of 2563 and 2553 Ma.

Zircons from the basement gneiss–greenstone components yield $^{207}\text{Pb}/^{206}\text{Pb}$ age of 3270 ± 3 Ma

(Mondal *et al.* 2002). The NW-trending mafic dykes post-date the giant quartz veins emplacement (Pati *et al.* 2007) and shear zone development (Basu 1986; Pati *et al.* 1997; Mondal and Ahmad 2001). Based on $^{40}\text{Ar}/^{39}\text{Ar}$ step heating ages, Rao *et al.* (2005) infer two phases of mafic dyke intrusion at 2000 and 2150 Ma although the inferences drawn are incorrect (Pati *et al.* 2010). These ages partly overlap with Rb–Sr isochron ages (2130 and 2402 Ma) from granitoids and tonalite-trondhjemite–granodiorite (TTG) suites (Sarkar *et al.* 1994, 1996).

The granitoids are traversed by regional east–west trending subvertical sinistral shear zones (figure 1), e.g., Raksa Shear Zone (~50 m wide; Senthippan 1976, 1981) and Bundelkhand Tectonic Zone (~up to 2 km thick; Pati 1998, 1999; Malviya *et al.* 2006; Pati *et al.* 2007, 2008b; Saha *et al.* 2010; Gokarn *et al.* 2013). The Bundelkhand Tectonic Zone has now been established as an Archean subduction zone (Malviya *et al.* 2006; Saha *et al.* 2010). Recent geochronological studies based on Ar–Ar step ages in parts of Bundelkhand craton have indicated the imprints of two possible hydrothermal/thermal events, at ca. 0.6 and ca. 1 Ga, synchronous with Pan-African and Grenvillian orogenies, respectively (Pati *et al.* 2010).

3. Mo mineralization in Archean Bundelkhand craton

The presence of Mo is observed in 23 locations during the present study in parts of Bundelkhand craton (figure 1). The majority of the Mo incidences cluster around $25^{\circ}15'$ (Bundelkhand Tectonic Zone) similar to gold mineralization reported by the first author earlier (Pati *et al.* 1997). However, some are observed in the vicinity of Raksa Shear Zone and others are associated EW-trending localized shear zones around Banda and Rauli Kalyanpur. Their strike continuities have not been mapped. The Mo mineralization in ABC mainly occurs as incidences in the form of films along shear planes (figure 2a), specks (figure 2b), stringers, pockets, and clots (table 1). Mo with or without other sulphide phases occurs in the visible form as massive clots (figure 2c), disseminated type (figure 2d), and as invisible type (mainly identified on the basis of oxidation haloes and/or brown coloured solution imprints; figure 2e). Mo films with Ccp are noted along the foliation surfaces of sheared granites (figure 2f). The disseminated types are observed in medium-grained granite associated with quartz. In Gonda area (table 1), Mo is found in the vicinity of a mesoscopic shear associated with Ccp. The massive Mo variety is mostly found in granite pegmatite veins intruding into the hornblende granite.

Figure 2. (a) Mylonitized pink granitoid with brownish haloes across the foliation and Mo films (open circle) occurring along the foliation surface are observed in this sample. The coin diameter is 2.5 cm. (b) Medium-grained pink granite (red circles) shows the presence of Mo in a linear pattern as clots. The coin diameter is 2.5 cm. (c) Mo with Py is seen to occur in quartz + feldspar-bearing granite pegmatite. The coin diameter is 2.5 cm. (d) An outcrop showing a medium-grained pink granitoid with disseminated Mo-specks (encircled with red pen; pen cap length: 3 cm) and brownish yellow oxidation haloes. (e) Medium-grained grey granitoid with brown coloured solution seams (after Mo) is seen pervasively in this outcrop. The molybdenite is only encountered in geochemical analysis. (f) Mo vein is exposed in a broken surface of medium-grained sheared pink granite. The coin diameter is 2.5 cm. (g) The massive Mo phase is seen to occur as clots in quartz without any other sulphide phase from a granite pegmatite rock. The coin diameter is 2.5 cm. (h) The molybdenite with brown oxidation haloes is seen to occur close to the interface of an intrusive contact between medium-grained pink granite and hornblende-bearing coarse-grained porphyritic granodiorite.

Table 1. Sample locations of the Mo-bearing rocks observed in parts of ABC and observed characteristics pertaining to their type of mineralization, mineral association and host lithology. Mineral abbreviations are after Whitney and Evans (2010).

Sl. no.	Location	Form of mineralization	Host rocks and structures	Association
1	Vishwaskhand Quarry (25°24'00"; 81°00'00"), Kabrai, Mahoba district	Pockets	Pegmatite (granite)	Mo + Apy
2	Lodha Pahar (25°23'30"; 80°00'20"), Kabrai, Mahoba district	Clots	Vein quartz in diorite mylonite	Mo + Py + Ccp + Bn
3	1 km E of Masuni (80°27'08"; 25°01'17"), Mahoba district	Specks	Mylonitized pink granite and pegmatite	Mo
4	Nasani Hill, Mahoba district	Disseminated type	Medium-grained pink granite	Mo
5	Bhuragarh (25°28'20"; 80°18'32"), Mahoba district	Disseminated type, films and clots	Fine-grained pink sheared granite	Mo + Ccp + Py
6	1.5 km ESE of Bijauli Railway Station (25°22'30"; 78°32'43"), Jhansi district	Disseminated type	Grey granitoid	Mo
7	Karin Pathar Pahar (25°11'52"; 80°42'5"), Banda district	Specks, clots and disseminated type	Foliated medium-grained pink granite	Mo + Py + Ccp
8	NE of Gonda (25°12'14"; 80°44'15"), Banda district	Stringers along shear plane	Foliated medium-grained grayish pink granite	Mo + Py + Ccp
9	WSW of Korari (25°11'01"; 80°44'15"), Banda district	Specks and clots	Foliated medium-grained grey granite	Mo
10	1.5 km N of Panihan Purwa (25°8'53"; 80°42'24"), Banda district	Specs and clots	Foliated medium-grained greyish pink granite	Mo
11	4 Locations over a strike length of ~800 m (SE and SW of Pahra, S of Kabrai) (25°21'41"; 80°04'20"), Mahoba district	Clots and Specks	Medium-grained grey granitoids	Mo
12	Daharra (~5 km ² area) (25°20'20"; 79°58'12"), Mahoba district	Invisible (12–25 ppm)	Medium-grained grey granitoids	Oxidation haloes are prominent
13	1.5 km SSW of Panara, Mahoba district	Clots	Porphyritic medium-grained grey granitoids	Oxidation haloes are present
14	50 m N of Babina–Nathikhera–Pritipur trijunction (25°12'00"; 78°31'03"), Jhansi district	Invisible (39 ppm)	TTG gneiss	Mo (earlier recovered from a nearby dug well section)
15	Chhikahra (25°21'41"; 79°51'42"), Mahoba district	Clots	Medium-grained grey granitoids	Mo
16	Gorahari Hill (25°27'00"; 79°37'00"), Mahoba district	Invisible (11 ppm)	Altered pink porphyritic granitoids	–
17	1.5 km NNE of Mankua, Jhansi district	Invisible (19 ppm)	Granitoid (ultramylonite)	–
18	1.25 m N of Dukwan IB, Jhansi district	Invisible (30 ppm)	Quartz (sheared)	–
19	1.37 km WNW of Hasarkhurd Temple, Lalitpur district	Invisible (52 ppm)	Quartz (sheared)	–
20	1 km NE of Ghosiana, Mahoba district	Invisible (35 ppm)	Quartz (sheared)	–
21	SE of Jharar Village (25°07'36"; 78°19'11"), Lalitpur district	Massive	Medium-grained pink porphyritic granitoids	Mo + Py + Ccp + Gn + Sp
22	Gugar area, Lalitpur district	Clots	Granitoid breccia body	Mo
23	Bela Sagar, Jhansi district	Films along foliation plane	Grey granitoids	Mo

Figure 3. (a and b) Representative photomicrographs obtained using plane polarized light in reflected light mode shows aggregates of molybdenite flakes in samples BHU-1 and BGM-9, respectively. In (a) majority of the grains are in the minimum absorption position (with a couple of them in orthogonal orientation). In (b) the grains are all in the maximum absorption (minimum reflectance) position. These aggregates of molybdenite flakes occur intimately associated with quartz within intergranular spaces as well as fracture fillings.

Figure 4. X-ray patterns of two representative samples (Mo-6 and Mo-7) using $\text{CuK}\alpha$ radiation between 10° and 40° (2θ) confirming the presence of molybdenite.

This variety is either observed within greasy quartz phase (figure 2g) occurring within pegmatite or in contact with hornblende granite with or without $\text{Py} \pm \text{Ccp}$. The clots are seen in biotite granite and along the contact between leucogranite and hornblende granite (figure 2h). The other associated sulphide phases observed include Py , Ccp , Bn and Cv (figure 2e) in Daharra–Pahara area. The mineralization is mostly localized except for the outcrop in Daharra–Pahara area.

4. Molybdenite characterization

Molybdenite is identified as bluish-grey coloured, very soft mineral having a metallic luster and greenish grey streak. It is flaky in nature and

easily peels off with pocket knife. Microscopic study shows euhedral to subhedral flaky aggregates with high reflectivity and blue anisotropism (figure 3a, b). The molybdenite flakes with one set of cleavage are intimately associated with quartz occurring within intergranular spaces as well as fracture filling. Other sulphide phases associated, wherever present, were physically separated under a stereozoom microscope and only molybdenite was analyzed by X-ray diffraction technique. Sulphide phases, in general, were analyzed by Electron Probe Micro-Analyzer (EPMA).

4.1 X-ray diffraction of molybdenite

Five molybdenite samples were separated under the microscope and analyzed by X-ray diffraction technique (Seifert X-ray Diffractometer, Lucknow University, India) using $\text{CuK}\alpha$ target and Ni filter and the 40 kV/30 mA operating condition. The calibration was carried out using Silicon standard. The major peaks at 2θ (14.48° , 44.22° and 49.95°) corresponding to their respective characteristic d-spacings (6.11, 2.05 and $1.83 \text{ \AA}$) were observed (figure 4). Mo occurs with or without other sulphide phases like pyrite (Py), arsenopyrite (Apy), chalcopyrite (Ccp), bornite (Bn), covellite (Cv), sphalerite (Sp) and galena (Gn) (Pati 1997; Shukla and Singh 1997; Nim and Hasan 1997).

4.2 Mineral chemistry of rock- and ore-forming minerals

The rock-forming minerals like feldspar, biotite, hornblende, muscovite, chlorite, sphene and epidote and ore-forming phases (Mo , Py , Ccp , Cv and Bn) were analyzed using Cameca Camebax

SX-51 system at the EPMA Laboratory of GSI, Faridabad. The presence of other reported sulphide phases (Sp and Gn) were not observed in the samples analyzed in this study. The analyses are summarized in table 2. Calibration is done using standards like natural silicate and oxide mineral from the BRGM, France and the data reduction is carried out after applying PAP correction (Pouchou and Pichoir 1985). Beam current and accelerating voltage were maintained at 20 nA and 15 kV, respectively.

The Mo-bearing granitoids show evidences of potassic alteration (secondary K-feldspar with secondary biotite associated with chlorite), phyllic alteration (vein quartz, sericite after feldspar chlorite and pyrite) and propylitic alteration (epidote, chlorite, calcite, sericite, and quartz). The feldspar composition is predominantly orthoclase-rich ($\text{Cn}_{1.4-1.8} \text{Or}_{93.8-96} \text{Ab}_{2.5-4.4}$) with significant barium molecule (Cn: celsian) and nearly pure albitic-end members ($\text{Or}_{0.7} \text{Ab}_{97.6} \text{An}_{1.7}$) are also present. In addition, both alkali feldspars and plagioclase ($\text{Or}_{0.5} \text{Ab}_{82.8} \text{An}_{16.7}$) feldspars are observed.

Predominantly the Mo-bearing granitoids of ABC are essentially two feldspar (sub-solvus; low temperature) granitoids. Biotite is Fe-rich ($\text{Fe}_{2.89}$) whereas chlorite contains only $\text{Mg}_{2.79}$ and is devoid of iron. Muscovite contains 2.19 wt.% total iron. Sphene has substantial titanium ($\text{Ti}_{0.80}$). The ore-forming minerals analyzed include Mo, Py, Ccp, Bn and Cv. Mo is nearly pure with trace of iron ($\text{Mo} = 60.65\text{--}61.58$ wt.%). The Au content in molybdenite should be ignored as the BRGM (France) Mo standard was Au-bearing. Presence of Py ($\pm$ Apy), Ccp (with Mo), and Cv (with Mo) have also been confirmed.

5. Petrology of molybdenite-bearing granitoids and related rocks

5.1 Petrography

The Mo occurs in variably deformed different petrological variants of granitoids. They include granitic pegmatites, coarse grained pink porphyritic

Table 2. The representative EPMA mineral analysis of rock-forming phases in Mo-bearing rocks in ABC. Mineral abbreviations are after Whitney and Evans (2010).

Mineral/oxide	Fs	Fs	Fs	Fs	Bt	Ms	Chl	Spn	Mag	Ep
SiO ₂	68.34	64.16	64.71	63.84	37.30	47.32	25.05	29.38	0.13	37.42
TiO ₂	0.20	0.00	0.00	0.00	2.59	0.04	0.11	31.23	0.09	0.07
Al ₂ O ₃	20.20	22.77	18.86	18.79	15.66	37.18	20.02	4.84	0.00	22.21
Cr ₂ O ₃	—	—	—	—	0.10	0.10	—	—	0.05	0.02
Fe ₂ O ₃	0.08	0.07	0.04	0.00	22.48	2.19	33.45	1.94	99.94	14.49
MnO	—	—	—	—	0.83	0.00	1.50	—	0.01	0.19
MgO	0.01	0.05	0.01	0.00	7.60	0.02	8.56	0.08	0.00	0.03
BaO	0.04	0.00	0.83	0.96	0.02	0.10	—	—	—	—
CaO	0.36	3.53	0.00	0.00	—	0.00	0.14	26.54	—	—
Na ₂ O	11.03	9.68	0.34	0.48	0.03	0.28	0.08	0.10	—	—
K ₂ O	0.10	0.09	15.11	15.38	9.15	8.24	0.05	0.02	—	—
H ₂ O ^C	—	—	—	—	3.89	4.57	10.95	0.72	—	0.93
Total	100.16	100.32	99.90	99.46	99.64	99.99	99.90	94.84	100.20	98.67
Si	2.977	2.821	2.990	2.977	5.742	6.201	5.483	1.000	0.005	0.005
Al	1.022	1.180	1.027	1.033				0.194	0.000	0.000
Al ^{IV}					2.258	1.799	2.517			
Al ^{VI}					0.582	3.944	2.648			
Fe ³	0.002	0.002	0.001	0.000				0.007	1.984	1.984
Fe ²					2.894	0.240		0.043	1.007	1.007
Ti	0.001	0.000	0.000	0.000	0.300	0.003	0.018	0.799	0.002	0.002
Mg	0.001	0.003	0.001	0.000	1.744	0.004	2.792	0.004	0.000	0.000
Na	0.931	0.825	0.031	0.043	0.010	0.072	0.035	0.007		
Ca	0.017	0.166	0.000	0.000	0.000	0.000	0.032	0.968		
K	0.006	0.005	0.891	0.915	1.796	1.377	0.014	0.001		
Ba	0.001	0.000	0.015	0.018	0.001	0.005				
Cn	0.001	0.000	0.014	0.018						
Or	0.006	0.005	0.960	0.938						
Ab	0.976	0.828	0.025	0.044						
An	0.017	0.167	0.000	0.000						

granitoids, medium grained grey granitoids, medium grained pink granitoids, and TTG mainly. However, Mo is noted in trace amount in sheared quartz also. The Mo-bearing rocks are in general holocrystalline, inequigranular, and medium-to-coarse grained (barring a pegmatitic variant). The minerals observed are: quartz (Qz), microcline (Mc), perthite, plagioclase (Pl), biotite (Bt), apatite (Ap), zircon (Zrn), sphene (Spn), ilmenite (Ilm), magnetite (Mgt), chlorite (Chl), epidote (Ep), sericite (Ser), opaque phase, and calcite (Cal). Qz phenocrysts are anhedral, invariably show undulose extinction and serrated grain boundaries with subgrain development (figure 5a). In places, ribbon Qz is also observed. Pl phenocrysts are subhedral to anhedral and invariably altered. Mc and perthite are mostly subhedral and relatively fresh. Bt are subhedral, prismatic, straw yellow to dark yellowish brown pleochroism and in places contain pleochroic halos as well. Spn with subhedral to euhedral shapes occurs mostly in the boundary between Bt and Ilm, possibly as a

reaction product. A fabric development in granitoids is very clear (figure 5b) which is either defined by Qz or Bt. The modal % of Qz (50–60), Or (40–30) and Pl (20–10) observed in Mo-bearing granitoids is variable.

5.2 Petrochemistry

The major and trace element analyses of 23 Mo-bearing rock samples and REE contents of eight samples are furnished in table 3. The samples were analyzed using XRF, ICP-AES, and INAA for their major, trace, and REE contents, respectively. The details of analytical methods, instruments, and calibrations are summarized in Pati et al. (2008b). The Mo-bearing granitoids of ABC with SiO₂ content between 68.18 and 76.41 wt.% (avg. 74.37; SD = 2.17) are fresh with LOI (loss on ignition) varying from 0.28 to 1.43 wt.% with mean value of 0.72 wt.% (figure 6a). The total alkali values range between 6.37 and 9.66 wt.% (avg.

Figure 5. (a) Mo-bearing granitoid defined by phanocrystalline anhedral texture and typical minerals (perthite + Qz + Pl + Mc + Ser) with a trace amount of Bt + Opq. Pl is partly altered and Mc is unaltered. (b) Mo-bearing sheared granitoid with perthite + Qz + Pl + Mc + Ms + Ser) with a trace amount of Opq. Qz grains show serrated grain boundaries, subgrain development and defines a penetrative fabric.

Table 3. Representative EPMA analyses of sulphide phases in Mo-bearing rocks in ABC. Mineral abbreviations are after Whitney and Evans (2010).

Mineral/element	Mo	Mo	Mo	Mo	Mo	Py	Py	Ccp	Cv
S	35.62	35.91	36.47	37.06	35.87	53.57	53.11	35.47	21.24
Fe	0.93	0.84	0.00	0.05	0.00	45.74	46.72	29.48	0.89
Cu	0.00	0.00	0.05	0.00	0.00	0.05	0.00	33.89	74.78
Zn	0.04	0.00	0.04	0.00	0.04	0.03	0.00	0.00	0.02
As	0.00	0.00	0.01	0.00	0.00	0.11	0.00	0.00	0.00
Mo	60.65	61.17	61.58	60.87	60.94	0.62	0.60	0.41	0.35
Ag	0.00	0.09	0.00	0.00	0.00	0.00	0.00	0.08	0.00
Au	0.36	0.51	0.22	0.53	0.44	0.03	0.00	0.00	0.00
Total	97.60	98.52	98.37	98.51	97.28	100.16	100.44	99.34	97.29

7.99; SD = 0.84) whereas the K_2O/Na_2O ratios lie between 0.43 and 2.09 (avg. 1.32; SD = 0.47) with six compositions having $Na_2O > K_2O$. The Al_2O_3 content in these samples lies within a restricted range (11.70–14.75 wt.%; avg. 12.79; SD = 0.83). They contain primary magnetite

($Fe_2O_3^T$: 0.47–4.6 wt.%; avg. 1.72; Sd = 1.08) with or without sphene. All major oxides barring K_2O show a decreasing trend with increasing SiO_2 (figure 6b–g) and the granitoids can be categorized into three broad groups within ~ 8 wt. SiO_2 . The compositions are metaluminous to peraluminous

Figure 6. (a) The LOI (loss on ignition) is minimal suggesting their largely unaltered nature in general. (b–g) Harker type variation diagrams of Mo-bearing rocks showing the variability of various oxides with respect to their respective SiO_2 contents. (h) The plot (Shand's index after Maniar and Piccoli 1989) shows the Mo-bearing rocks to metaluminous to peraluminous in nature. (i) The normative analysis of Mo-bearing rocks are plotted in terms of quartz-albite-K-feldspar (Q–Ab–Or) and the eutectic composition from various experimental runs are also plotted (redrawn after Winter 2001). (j) Ta–Yb (after Pearce *et al.* 1984) shows that the Mo-bearing granitoids of the ABC are volcanic arc granitoids (VAG). (k) The primitive mantle normalized multiplication parameter diagram (after Sun and McDonough 1989) shows the Mo-bearing granitoids to have high Th, Pb, K and La contents and characteristically depleted in Nb, Ta and Ti. (l) The chondrite normalized REE pattern (after Sun and McDonough 1989) shows a typical LREE-enriched, HREE depleted and varied Eu-anomaly.

Figure 6. (Continued.)

(figure 6h). The normative analyses of granitoids are plotted in Q–Ab–Or phase diagram (figure 6i) showing change in ternary eutectic and minimum compositions with variable water pressure, anorthite, boron, and fluoride contents (modified after Winter 2001). The compositions largely plot within worldwide granitic compositional field. The K_2O – SiO_2 diagram suggests that these Mo-bearing granitoids belong to high-K (Calc-alkaline) series. The Na_2O – K_2O diagram used to discriminate I-, A- and S-type granitoids

(Collins *et al.* 1982) when employed for our Mo-bearing granitoids, indicate both I- and A-type affinity. The Yb–Ta tectonic discrimination plot suggests these compositions to be volcanic arc granites (figure 6j). The Rb/Sr values range between 0.49 and 5.68 ($n=15$; avg. 1.95; SD = 1.50) suggesting the granitoids reached only low to moderate degree of fractionation. Hence, the K-feldspar-bearing granitoids from the ABC may have crystallized from a residual mafic melt after differential crystallization. The granitoids

associated with Mo-mineralization have a high Rb/Sr content (Plimer and Elliott 1979). The SiO_2 -Rb/Sr (after Tischendorf and Pälchen 1985) suggests that these granitoids are *in-situ* formed crustal granitoids and occur in the W-Mo mineralized granite field of Raith (1995). The rock/primitive mantle normalized multicationic parameter diagram (after Sun and McDonough 1989; figure 6k) shows Rb, Ba, and Pb enrichment along with K whereas Sr, Ti, and HREE are relatively depleted. The subduction-related crustal compositions are characteristically enriched in silica and LIL elements (K, U, and Pb) and depleted in incompatible elements (Nb, Ta, and Ti) (Stern and Scholl 2013). In addition, the K-feldspar-bearing granitoids with Bt are known to contain Rb and Ba in substantial amount and K-feldspar is a potential carrier of Pb (Ewart and Griffin 1994). Hydrothermal solutions can carry Pb as well and Pb can be highly mobile in metamorphic fluids (Wedepohl 1974). The normalised REE data (after Sun and McDonough 1989) of eight samples (table 3) show a LREE enriched and HREE depleted fractionated pattern with or without Eu anomaly (figure 6l). This is consistent with the fractionated pattern shown by alkali-feldspar-bearing Bundelkhand granitoids, even though these samples have varied total REE concentrations.

6. First data on fluid characteristic of Mo-bearing quartz grains and veins

Four samples (BNS-84, BNS-106, BHU-1, and BGM-9) containing visible Mo intimately associated with quartz were studied for their fluid

inclusion characteristics using a Linkam THMSG 600 heating-freezing stage mounted on a Leica (DMLM) digital polarizing microscope with camera attachment at the Department of Geology and Geophysics, IIT, Kharagpur. Inclusion petrography revealed presence of aqueous biphasic inclusions as the most dominant type in all samples.

Aqueous-carbonic inclusions were observed in good numbers in samples BNS-84 and BNS-106 (figure 7a, b). Primary inclusions were well preserved with mild effects of later deformations (stretching of large inclusions). Non trail-bound moderate sized inclusions with regular shapes and away from healed cracks were chosen for microthermometry and the fluid inclusion data are summarized in figure 8(a, b, c, d). In all, inclusions from all four samples together furnish a salinity range of ~1 to 31 wt.% NaCl equivalent without a prominent mode, though salinity range of 1 to 4 wt.% NaCl equivalent slightly outnumber inclusions in other ranges. There is a uniform representation of inclusions in the range of 4–24 wt. NaCl equivalent, classed at 4 wt.% interval. This indicates a mixing trend between fluids of high and low salinities. Temperatures of homogenization obtained also vary between 100° and 309°C, again without a distinct mode. However, most homogenization temperatures are clustered between 150° and 230°C. A uniform representation of inclusions in all temperature intervals and clustering in a restricted range is corroborative evidence in favour of mixing of fluids. Paired salinity- T_h diagram also favours a mixing model with linear clustering parallel to the salinity axis. This trend indicates mixing of fluids of contrasting salinity without much of a contrast in their temperatures (figure 8c).

Figure 7. The aqueous biphasic inclusions in two representative samples of Mo-bearing quartz veins. The samples are from BGM 9 (a) and BNS 106 (b), respectively. They all occur as part of the three dimensional network interpreted to be primary. Photographs show the inclusions in focus with others at different planes. The figures show more or less uniform fluid inclusion characteristics across samples in the area.

Figure 8. Characteristics of aqueous fluids associated with molybdenite mineralization in the study area. (a) Histogram of salinity in wt.% NaCl equivalent; (b) histogram of temperature of homogenization; (c) fluid evolution diagram using temperature-salinity and (d) fluid evolution diagram using temperature density values.

There has been continued attempt to understand the hydrothermal geochemistry of molybdenum in relation to its transport and deposition. Keeping in view that the majority of Mo deposits are associated with granitic rocks, a strong affinity of the metal to felsic melts is expected. Isuk and Carman (1981) measured solubility of Mo in silicate melt and suggested that the metal is possibly carried in the melt as $\text{MoSi}_2\text{O}_5^{2+}/\text{MoSi}_2\text{O}_6/\text{MoSi}_2\text{O}_4(\text{OH})^{3+}$ species. However, since transport in fluid medium is a prerequisite for formation of its deposit, the mechanism of transport, or more specifically, the complexing ligand must be understood. Unlike copper (the metal with which it is closely associated) which has a strong affinity for chloride ion, molybdenum is known to form oxyhydroxo complexes (Candela and Holland 1984) and the concentration of Mo is understood to be independent of chloride content of the fluid. Webster (1997) determined the apparent melt *versus* fluid partition coefficient of 8–80 for molybdenum

as a function of NaCl+KCl content of fluid, yet suggested that Mo is not transported as chloride complex. Ulrich and Mavrogenes (2008) observed that the type of complexing varies with fluid chemistry. They suggested that Mo could be transported either as $(\text{K}/\text{Na}) \text{HMoO}_4$ or $\text{MoO}_2\text{Cl}^+/\text{MoO}_2\text{Cl}_2/\text{MoO}_2\text{Cl}_3^-$ (depending on the Cl^- concentrations) in fluids with high to moderately high salinity. In low saline water rich fluid, the Mo transport efficiency is reduced although H_2MoO_4 type species could still be present. Such a mode of transport is in good agreement with the present study in which a Na–K-rich host pluton would have initially carried molybdenum. On magmatic-hydrothermal transition, the K–Na-rich fluid, represented by the moderate to high saline fluid would have continued transporting Mo and deposited in response to mixing with low-saline fluid. Panigrahi and Mookherjee (1997) also suggested transport of both Cu and Mo in the same fluid and concluded deposition as a result of mixing of fluids.

Table 4. The representative major, trace and REE analyses of Mo-bearing rocks of the ABC. Major element analyses are in weight % and trace elements including REEs are in ppm.

Sample/oxide	BM-1	BM-2	BM-3	BM-4	BM-5	BM-6	BM-7	BM-8	BM-9	BM-10	BM-11	BM-12
SiO ₂	74.32	75.57	75.64	75.72	70.44	76.41	70.36	76.18	74.51	73.41	74.49	75.77
TiO ₂	0.10	0.02	0.11	0.07	0.19	0.07	0.07	0.04	0.11	0.03	0.12	0.04
Al ₂ O ₃	13.22	13.29	13.32	12.93	14.3	12.93	14.75	12.31	12.6	13.20	12.30	12.6
Fe ₂ O ₃	1.83	0.47	1.54	1.25	3.70	1.25	2.70	1.11	1.30	0.85	0.92	0.79
MnO	0.02	0.01	0.01	0.01	0.04	0.01	0.01	0.01	0.02	0.01	0.02	0.01
MgO	0.40	0.11	0.65	0.18	1.12	0.18	1.04	0.22	0.86	0.51	0.57	0.48
CaO	0.35	0.65	0.25	1.13	2.20	1.13	1.30	0.63	0.40	0.26	0.44	0.39
Na ₂ O	3.97	3.47	3.74	4.60	4.44	4.60	4.66	3.87	3.27	3.08	3.27	2.93
K ₂ O	4.84	6.19	4.59	3.32	1.93	3.32	3.56	5.09	4.70	5.70	4.80	6.00
P ₂ O ₅	0.11	0.02	0.07	0.01	0.27	0.01	0.27	0.01	1.40	1.58	2.19	0.09
LOI	0.47	0.55	0.33	0.56	0.97	0.56	1.43	0.65	0.59	1.26	0.89	0.36
Total	99.63	100.33	100.25	99.78	99.6	100.47	100.15	100.12	99.76	99.89	100.01	99.46
V	n.d.	<10	<10	<10	34	29	43	26	<10	<10	<10	27
Cr	3.6	11	<10	<10	28	27	20	17	<10	<10	<10	17
Co	1.8	<5	<5	<5	<5	<5	7	<5	<5	<5	<5	5
Ni	20	20	20	23	27	26	23	23	20	18	20	27
Cu	<10	7	13	11	11	11	11	22	6	9	8	5
Zn	15	27	25	25	53	46	70	42	24	21	24	50
Rb	n.d.	180	210	155	170	155	135	160	245	235	220	165
Sr	n.d.	87	99	99	150	146	275	184	114	96	124	156
Y	n.d.	<20	32	<20	32	26	20	<20	33	27	33	25
Zr	n.d.	139	150	147	285	269	331	246	189	119	185	258
Nb	n.d.	28	34	29	31	30	24	27	31	35	31	30
La	25	14	27	45	80	60	22	33	n.d.	n.d.	n.d.	n.d.
Ce	32	20	64	80	119	100	37	17	n.d.	n.d.	n.d.	n.d.
Sm	2.5	1.6	4.1	4.5	5.5	5.2	3.2	2.2	n.d.	n.d.	n.d.	n.d.
Nd	11	8.4	22	37	36	38	15	9	n.d.	n.d.	n.d.	n.d.
Eu	0.73	0.51	0.52	1.33	1.1	1.7	0.66	0.7	n.d.	n.d.	n.d.	n.d.
Tb	0.38	0.14	0.64	0.57	0.52	0.75	0.52	0.38	n.d.	n.d.	n.d.	n.d.
Yb	0.69	0.35	1.1	0.51	0.94	1	0.61	1	n.d.	n.d.	n.d.	n.d.
Lu	0.09	0.05	0.12	0.05	0.12	0.19	0.08	0.1	n.d.	n.d.	n.d.	n.d.
	BM-13	BM-14	BM-15	BM-16	BM-17	BM-18	BM-19	BM-20	BM-21	BM-22	BM-23	
SiO ₂	75.60	75.85	76.10	73.52	72.73	68.18	73.32	75.79	76.29	75.80	74.40	
TiO ₂	0.12	0.07	0.10	0.28	0.25	0.44	0.24	0.14	0.06	0.14	0.23	
Al ₂ O ₃	12.30	11.70	12.00	12.30	12.50	14.60	12.40	11.90	12.10	12.20	12.50	
Fe ₂ O ₃	1.10	0.89	1.00	3.10	2.80	4.60	2.60	1.10	1.00	1.00	2.60	
MnO	0.02	0.02	0.02	0.05	0.05	0.08	0.05	0.02	0.02	0.02	0.05	
MgO	0.73	0.61	0.53	0.69	0.84	1.00	0.80	0.39	1.00	0.55	0.49	
CaO	0.29	0.47	0.47	1.80	1.60	3.30	1.70	0.15	0.77	0.51	1.90	
Na ₂ O	3.00	3.26	3.12	3.26	3.26	3.88	3.31	2.68	3.00	3.05	3.44	
K ₂ O	5.30	4.90	4.90	3.80	3.90	2.60	3.70	5.60	5.10	5.50	3.30	
P ₂ O ₅	0.89	0.92	0.79	0.63	0.64	1.21	0.61	0.93	0.91	0.87	0.56	
LOI	0.68	0.75	0.90	0.51	0.94	0.93	0.78	0.86	0.28	0.52	0.75	
Total	100.03	99.44	99.93	99.94	99.51	100.82	99.51	99.56	99.53	100.16	100.00	
V	<10	<10	<10	34	29	43	26	<10	<10	<10	27	
Cr	11	<10	<10	28	27	20	17	<10	<10	<10	17	
Co	<5	<5	<5	<5	<5	7	<5	<5	<5	<5	5	
Ni	20	20	23	27	26	23	23	20	18	20	27	
Cu	7	13	11	11	11	11	22	6	9	8	5	
Zn	27	25	25	53	46	70	42	24	21	24	50	
Rb	180	210	155	170	155	135	160	245	235	220	165	

n.d.: not determined.

Table 4. (Continued.)

Sample/oxide	BM-13	BM-14	BM-15	BM-16	BM-17	BM-18	BM-19	BM-20	BM-21	BM-22	BM-23
Sr	87	99	99	150	146	275	184	114	96	124	156
Y	<20	32	<20	32	26	20	<20	33	27	33	25
Zr	139	150	147	285	269	331	246	189	119	185	258
Nb	25	34	29	31	30	24	27	31	35	31	30

7. Conclusions

The mesoscopic, microscopic and submicroscopic physico-chemical characterization of metallic phases confirm the presence of molybdenite with or without Py $\pm$ Ccp $\pm$ Bn $\pm$ Gn $\pm$ Sp $\pm$ Ep $\pm$ Cal. The Mo-bearing rock types include granite pegmatite, granite, granodiorite and TTG gneisses, mainly. The mineralization is mostly associated with sheared granitoids and predominantly occurs along/around the Bundelkhand Tectonic Zone and Raksa Shear Zone coinciding largely with the trend observed in case of gold mineralization earlier reported (Pati et al. 1997) from the ABC. The granitoid geochemistry suggests that the Mo-bearing rocks are high-K, metaluminous to peraluminous, moderately fractionated, volcanic arc-generated, I- and A-type granitoids and occur in the W-Mo mineralized granite field of Raith (1995). The porphyry Cu-Mo mineralization is generally known to be associated with metaluminous granitoids (McMillan and Panteleyev 1980) similar to the Mo-bearing granitoids of the ABC. The Mo mineralization in granitoids mainly occurs in the form of specks, disseminated type, clots, stringers, solution seams, and as films. The Mo (visible and invisible) with or without other sulphides occurring along the shear planes as films, fault traces, intrusion lobes and pegmatite veins, and different granitoid variants suggest the mineralization to be a polyphase temporal event although the chronological data is currently unavailable.

The first fluid inclusion data from different sample types and areas obtained during the present study indicate a dominantly aqueous hypersaline fluid homogenized at moderate temperatures (100–300°C) advocating a possible hydrothermal origin for the Mo-bearing quartz vein although more microthermometric data are needed to address the issue of molybdenum transport and deposition. Varied fluid types, mixing, and different homogenization temperatures also support multiple phases of mineralization in contrasting thermo-tectonic settings in parts of the ABC.

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