JOURNAL GEOLOGICAL SOCIETY OF INDIA
Vol.92, October 2018, pp.393-403

Geochemical Evidences for Possible Absence of Cu-Sulfide Deposits in the Deccan Volcanic Province, India

More B. Laxman and K. Vijaya Kumar*
School of Earth Sciences, SRTM University, Nanded – 431606, India
E mail:_vijay_kumar92@hotmail.com_

ABSTRACT

Continental flood basalt provinces (CFBs) are important hosts for large-scale Cu-sulfide deposits. However, sulfide mineralization is yet to be discovered, if any, in the end-Cretaceous Deccan volcanic province, India. In the present study, geochemical evidences for the possible absence of Cu-sulfide deposits associated with the Deccan basalts by analyzing and comparing the geochemistries of the Deccan and Siberian CFBs are provided. The Fe-rich nature and high fO_2 conditions did not favour sulfide saturation at any stage of magma evolution in the Deccan province. Crustal contamination of the Deccan magmas also did not increase the sulfur budget. The most contaminated basalts of Bushe and Poladpur formations of the Deccan province do not show any depletion in the copper contents compared to other formations. In the absence of sulfide saturation, copper behaved as an incompatible element in the Deccan magmas in contrast to the Siberian basalts, in which copper behaved as a compatible element during magma evolution due to sulfide saturation consequently formed world-class copper sulfide deposits. It is demonstrated that the lithosphere- and asthenosphere-derived Deccan magmas have similar Cu abundances thereby suggesting that the Cu-sulfide deposits associated with the CFBs are process-controlled rather than source-controlled. Although Cu-sulfide deposits may not have formed, the geochemical patterns suggest favourable conditions for native copper mineralization in the Deccan volcanic province. In the present study, a set of geochemical proxies that can be utilized as preliminary exploration tools for Cu-sulfide mineralization in the CFBs is proposed.

INTRODUCTION

Copper sulfide ore formation in continental flood basalts (CFBs) is a much-debated topic in the realm of magmatic ore deposits. Some of the CFBs designated as “fertile provinces” are hosts to large-scale Cu, Ni and PGE sulfide deposits (for example Siberia, Emeishan, Tarim, Karoo provinces; Zhang et al., 2008); however, some other CFBs designated as “barren provinces” are devoid of sulfide deposits (for example Deccan, Parana, Ferrar provinces; Zhang et al., 2008). Zhang et al. (2008) and Griffin et al. (2013) argued that the ancient cratonic lithospheres contributed substantially to the budget of Cu and Ni to the plume magmas, which eventually formed large sulfide deposits associated with the fertile CFBs; whereas in the barren CFBs, sub-continental lithosphere contribution was minimal. Alternately, Lee et al. (2012) suggested that copper abundances are not distinctly different in the plume-, arc- and ridge-derived primary basaltic magmas consequently inferred that the ore deposit formation is linked to magma evolution process rather than mantle source and primary melt compositions.

In either case (*source-controlled* or *process-controlled*), ultimate formation of the sulfide deposit requires concentration of the ore and its separation from the silicate fraction. Factors that influence sulfur-saturation of the magma and physical segregation of sulfide minerals include (1) degree of mantle melting, (2) FeO, SiO_2 and Na_2O+K_2O contents in the magma, (3) fO_2 and fS_2 fugacities, (4) P-T conditions, (5) assimilation of crustal sulfur and (6) liquid immiscibility. Moderate degrees of mantle melting (~ 20%) produce highest amount of sulfur in the melt (Keays, 1995; Arndt et al., 2005). At lower degrees of melting sulfide phase would be in mantle residue and higher degrees of melting results in the dilution of sulfur in the melt (Wendlandt, 1982; Keays, 1995; Rehkämper et al., 1999). Lower concentration of FeO, high concentrations of SiO_2, Na_2O + K_2O are favourable for sulfide ore formation (MacLean, 1969; Haughton and Roeder, 1974; Buchanan and Nolan, 1979; Naldrett, 2004). Sulfur content needed for sulfide saturation increases exponentially with fO_2 (Jugo et al., 2005; Jugo, 2009). It was estimated that 1300 ppm S is sufficient to induce sulfide saturation at FMQ-1 and 1500 ppm at FMQ+1 for MORB; 7500 ppm at FMQ+2 for back-arc and ocean island basalts and can be as high as 1.4 wt.% at FMQ+2.3 for island-arc basalts (Jugo, 2009). At FMQ+2 conditions, most of the sulfur occurs in sulfate state which has 10 times higher solubility than sulfide (Carroll and Rutherford, 1987; Jugo et al., 2005; Mungall et al., 2006; Jugo, 2009). High temperature magmas dissolve higher amounts of sulfur (Naldrett, 2004; Barnes and Lightfoot, 2005) whereas decreasing pressure increases S solubility in the magma (Mavrogenes and O’Neil, 1999). Therefore, rapid adiabatic ascent of the magma would shift the magmas into the field of sulfur undersaturation (Mavrogenes and O’Neill, 1999) thereby inhibits sulfide ore formation. Crustal contamination is a key process which brings S-undersaturated tholeiitic basaltic magmas to S-saturation and subsequent sulfide ore formation (Brugmann et al., 1993; Wooden et al., 1993; Lightfoot et al., 1990, 1993 and 1994; Hawkesworth et al., 1995; Naldrett et al., 1992, 1995; Lightfoot and Keays, 2005). Assimilation of crustal material is a crucial factor in sulfide saturation because it will influence temperature, SiO_2, Na_2O+K_2O and also adds sulfur to the magma. Solubility of sulfide in mafic-ultramafic magmas decreases with increasing $aSiO_2$ and aNa_2O (MacLean, 1969). Addition of sulfur from the crustal sources to the mantle-derived magmas aids to raise sulfur saturation to the levels at which sulfide segregates (Naldrett, 1999; Naldrett et al., 1992; Lesher and Campbell, 1993; Ripley et al., 2002; Arndt et al., 2005; Lightfoot and Keays, 2005; Wilson and Churnett, 2006). The relationship between assimilation of crustal sulfur by parental magmas and segregation of magmatic sulfides is well recognized in Noril’sk-Talnakh, Voisey’s bay and Tarim Basin (Naldrett, 1999).

One geochemical feature that is firmly established in the CFBs is chalcophile element (Cu, Ni, PGE) depletion in silicate magmas (basalts) associated with sulfide ores (Brugmann et al., 1993; Czamankse et al., 1994; Fedorenko, 1994; Lightfoot et al., 1994; Lightfoot and Keays, 2005). The erupted basalts, equilibrated with sulfide ore, are supposed to show chalcophile depletion whether sulfide saturation took place in large deep magma chambers (Brugmann et al., 1993), in narrow shallow magma chambers (Rad’ko, 1991; Naldrett

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et al., 1995) or in magma conduits (Naldrett et al., 1992). In general, basalts directly associated with the deposits are considered to test this hypothesis; however, it is also possible that the basalts equilibrated with sulfide deposits may migrate to far-off distances. In such a scenario, considering complete data on a regional scale is the best possible approach to decipher chalcophile element behaviour with respect to sulfide saturation, if any, at any stage during magma differentiation.

Large deposits of copper (sulfide or native) are yet to be reported from the Deccan volcanic province (DVP), which covers ~5,00,000 km^2 area of the Indian subcontinent. Two possible reasons for the non-discovery of copper sulfide deposits in the DVP include: (1) the sulfide deposits were formed but not exposed to the surface or (2) the deposits did not form. Keays and Lightfoot (2010) suggested that the sulfides of copper and other chalcophile elements did not form in the DVP because the magmas were not saturated in sulfur. Zhang et al. (2008) contended that the lithosphere beneath the Deccan did not contribute enough chalcophile element budget to the plume-derived magmas to constitute ore deposits. In a recent study, Krishnamurthy (2015) argued for the possibility of the Deccan basalts hosting large-scale copper sulfide deposits.

In the present study, new geochemical evidences for *possible* absence of copper sulfide deposits in the Deccan volcanic province are provided. The predictive models proposed are based on *available* Cu abundance data on the erupted Deccan basalts and intrusives. Based on presently available data the model predicts that the *possibility* of having Cu-sulfide deposit in the DVP *is less*. The discovery of any copper sulfide deposit in DVP do not negate the model, it only suggests lack of relevant data in the available dataset. The mechanism of copper sulfide ore formation on the basis of behaviour of geochemical proxies during magma evolution is evaluated. The geochemical proxies utilized in the present study can be tested as preliminary exploration tools for Cu-sulfide mineralization in the CFBs. The Siberian and Deccan volcanic provinces have been considered – the former hosts world-class Cu-sulfide deposits and Cu-sulfide deposits are yet to be discovered, if any, in the latter– to constrain the favourable conditions for Cu-sulfide ore formation in the continental flood basalt provinces.

Major and trace element data for the Deccan and Siberian volcanic provinces from the GEOROC database have been compiled. The data was filtered and analyzed for geochemical accuracy and only data on magmatic rocks of basaltic composition (MgO > 4 wt.%) are considered in the present study. Samples that were analyzed prior to 1970 were not considered in the analysis. Almost all the Siberian basalts considered in the present study come from Noril'sk region. Distribution of selected basalts, from the GEOROC database, in the Deccan volcanic province is shown in Fig.1. In the Deccan province region-wise analysis of geochemical variation is carried out and found that there is no region-dependent Cu variation. The Cu contents in the intrusive rocks associated with Deccan basalts have also been compared. Once again there is no region-wise distinction. The only difference found was that basalts with high Cu abundances (possibly in native state) are more dominant in the northern DVP compared to southern DVP.

DECCAN AND SIBERIA VOLCANIC PROVINCES

At the K-T boundary (65-66 Ma), the Indian subcontinent experienced enormous magmatism within a short period (Courtillot et al., 1986, Duncan and Pyle,1988; Venkatesan et al., 1993; Baksi, 1994, Allegre et al.,1999) constituting Deccan volcanic province (DVP). The Deccan basalts were erupted predominantly on the heterogeneous Archean and Proterozoic crust of the Indian shield, and Phanerozoic epicontinental carbonate rocks and coal seams (Chakrabarti and Basu, 2006; Ray et al., 2008; Krishnamurthy, 2015). The Deccan traps

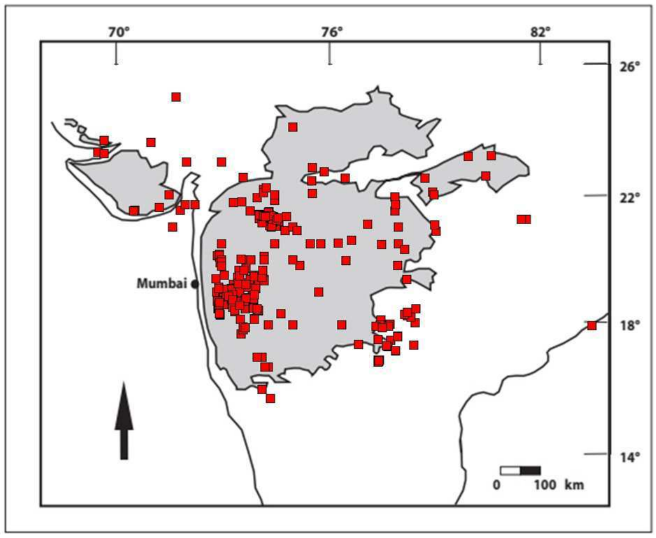

Fig. 1. Sketch map of the Deccan volcanic province with distribution of basalts considered in the present study from the GEOROC database (georoc.mpch-mainz.gwdg.de/georoc/).

presently cover an area >$5x10^5$ km^2, but originally might have erupted over an area of $1.5x10^6$ km^2 (Wadia, 1975). High rate of eruption within short period of time (1km^3/Year) is suggested for the DVP, which is very high compared to present day Hawaiian volcanism (0.1 km^3/Year) and other flood basalts (Courtillot et al., 1986). The Deccan volcanism was initiated by continental rifting during the final phases of the Gondwana fragmentation (Segev, 2002) at around 65±1 Ma. The continental-rifting was caused by either lithospheric stretching (e.g., Sheth, 2005) or plume impinging (Courtillot et al., 2003; Jerram and Widdowson, 2005; Vijaya Kumar et al., 2018). The western margin of the Deccan CFB is considered to be a major locus of eruptive centers (e.g., Raja Rao et al., 1978; Beane et al., 1986). The thickness of the Deccan traps decreases from west (>2000 m) to east (<100 m) as controlled by location of eruptive centers and pre-Deccan topography (Mahoney et al., 2000; Jay and Widdowson, 2008).

The Deccan primary picritic to basaltic melts are formed by 20 to 1% of melting of the mantle sources (Vijaya Kumar et al., 2018). The geochemical variation in the Deccan basalts can be modeled by different degrees of melting of the mantle followed by fractional and assimilation fractional crystallization of the primary liquids (Vijaya Kumar et al., 2010 and 2018). The age corrected εNd_i in the Deccan basalts ranges from -18 to +7 indicating multiple mantle sources and large scale crustal assimilation (Vijaya Kumar et al., 2018). Based on εNd_i values, it is estimated that lithosphere and sublithosphere (plume and/or E-MORB patches within asthenosphere) have contributed, respectively, approximately 36 and 64% to the southern Deccan volcanic province and 31 and 69% to the northern Deccan volcanic province (see Vijaya Kumar et al., 2018). There are no known copper sulfide deposits associated with erupted basalts or sub-volcanic intrusions in the Deccan province.

The 248±4 Ma old Siberian basalts were erupted on platform sediments including marine dolomites, calcareous and dolomitic marlstones, argillites and sandstones, and sulfate-rich evaporates (Naldrett, 1992; Czemanske et al., 1994). It is suggested that the Siberian basalt parental magmas were generated at much shallower depths and for much lesser degrees of partial melting than the magmas that produced the Deccan basalts (Keays and Lightfoot, 2010). In the Siberia province the ore-bearing Noril'sk Complex comprises differentiated (Av. MgO = 10–12 wt.%) intrusions, which host disseminated and stringer–disseminated ores localized close to contacts of intrusions with country rocks (Krivolutskaya et al., 2011 and

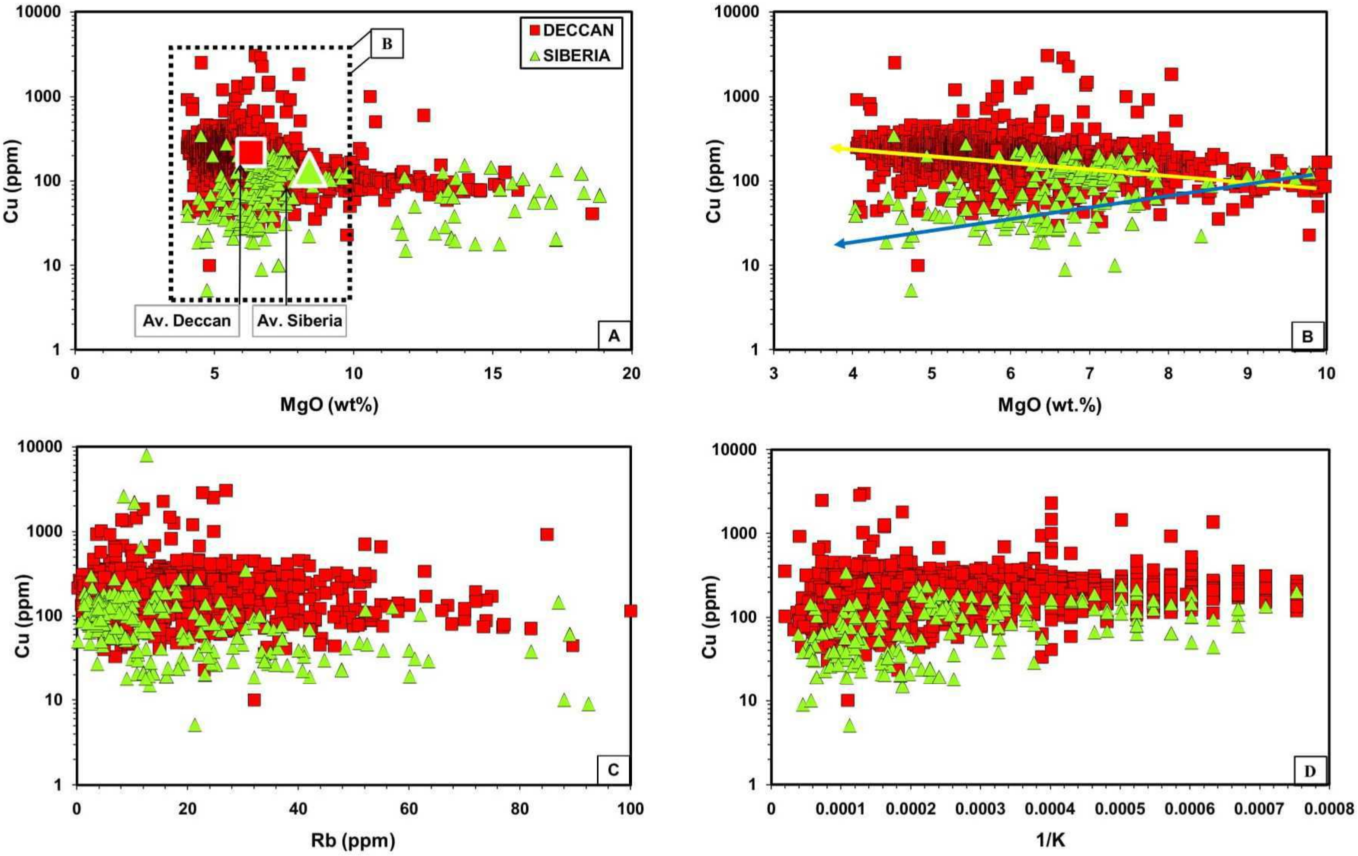

Fig. 2. Cu (ppm) *vs.* MgO (wt.%) (**A** and **B**), Cu (ppm) *vs.* Rb (ppm) (**C**) and Cu (ppm) *vs.*1/K (**D**) variations in the Deccan and Siberian continental flood basalts (samples with > 4% MgO are considered in the present study). Note higher copper abundances in Deccan compared to Siberian basalts. Average MgO and Cu abundances for Deccan and Siberia basalts are also shown. Geochemical data used in this and all other figures was mainly extracted from the GEOROC database maintained by the Max Planck Institute für Chemie in Mainz, Germany (georoc.mpch-mainz.gwdg.de/georoc/).

references therein). The Siberian sulfide deposits are considered to have formed by contamination of anhydrite-bearing sedimentary rocks at shallow depths (Campbell et al., 1992; Naldrett et al., 1992).

COPPER IN THE DECCAN AND SIBERIAN BASALTS

Geochemical data suggests that Deccan traps have higher abundances of copper (Av. abundance = 217 ppm) than Siberian flood basalts (Av. abundance = 135 ppm) (Fig. 2A). Some of the Deccan basalts contain few thousand ppm of copper. In both the provinces primary liquids (MgO>20 wt.%) have similar Cu concentration (Fig. 2A) but with magma evolution the Deccan and Siberian basalts show distinctly different variation trends. In the Deccan basalts copper steadily increased with decreasing MgO (Figs. 2A and B; Keays and Lightfoot, 2010). Whereas in the Siberian basalts copper shows a decreasing trend with decreasing MgO, especially from MgO = 10 wt.% onwards (Figs. 2A and B). Similar relationships are recorded in Rb-Cu and 1/K-Cu variation plots. The Deccan basalts show flat to slightly increasing trends whereas the Siberian basalts show decreasing trends for Cu with increasing Rb (Fig. 2C) and decreasing 1/K (Fig. 2D).

GEOCHEMICAL PROXIES INDICATING COPPER SULFIDE MINERALIZATION

Copper sulfide deposits generally form in the feeder conduits or shallow magma chambers (Lesher et al., 1981; Naldrett et al., 1995; Maier et al., 2001; Yuan et al., 2012), thereby depleting copper contents in the associated silicate magmas (see Yuan et al., 2012). If the conduit system is open to continuous magma replenishment and its interaction with immiscible sulfides then the associated basalts have higher levels of depletion in chalcophile elements (Zang et al., 2009). Cu/Zr ratios are used as geochemical proxies to infer Cu-sulfide ore formation in the CFBs (Naldrett et al., 1995; Naldrett et al., 1996; Li and Naldrett, 1999). In the basaltic magmas both copper and zirconium are incompatible elements (D<1) and have comparable bulk distribution coefficients; whereas copper has much higher distribution coefficient than zirconium in the sulfide minerals (Ripley et al., 2002). Therefore, it is possible to detect the involvement of sulfide minerals in the fractionating mineralogy using Cu/Zr ratios (Naldrett and Lightfoot, 1993; Stanton, 1994; Keays and Lightfoot, 2010; Nadeau et al., 2013). If the magma differentiation is only by silicate minerals then Cu/Zr ratio does not change or slightly increases (since $D_{Cu} \leq D_{Zr}$) with magma evolution. However, if sulfides start forming and fractionating then Cu/Zr ratio drastically decreases with magma evolution. MgO content is used as the monitor of magma evolution. The Siberian basalts have much lower Cu/Zr than the Deccan basalts at given MgO contents and show contrasting differentiation trends (Fig. 3). It is evident that in the Deccan basalts Cu/Zr increases with decreasing MgO whereas in the Siberian basalts Cu/Zr ratio decreases with decreasing MgO i.e., with magma evolution (Fig. 3). Two magma series [high MgO (24-11 wt.%) and low MgO series (10-4 wt.%)] are exhibited by the Siberian basalts (Fig. 3B). Although, both the series of the Siberian basalts show decreasing trends, decrease in Cu/Zr ratio is more prominent in the low MgO series (Fig. 3B). Some of the Deccan basalts have Cu/Zr ratios >10, possibly due to presence of native copper in those basalts. Some of the Deccan basalts do show Cu/Zr ratios <1 (Figs. 3A; Krishnamurthy, 2015); however, this is possibly due to

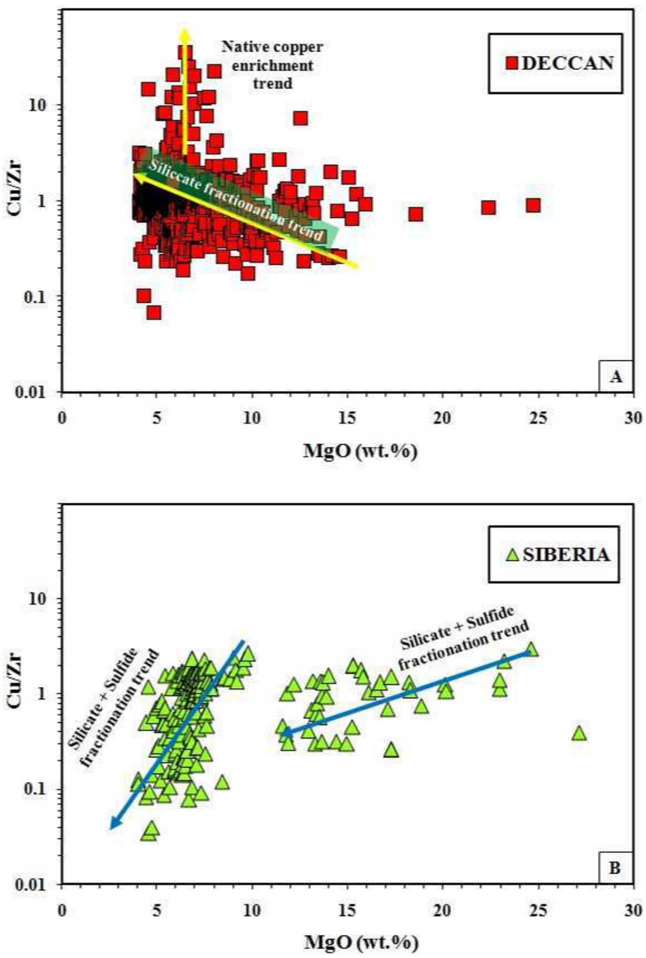

Fig. 3. Cu/Zr *vs.* MgO (wt.%) variations in the Deccan (**A**) and Siberian (**B**) continental flood basalts. Note distinctly different variation trends in the Deccan and Siberian basalts.

higher Zr rather than lower Cu (Cu = >40 ppm; Fig. 4). Oxide-rich basalts have higher bulk distribution coefficients for Zr than Cu, therefore they tend to contain more Zr consequently lower Cu/Zr ratios. Only 6 out of 1549 Deccan basalts considered in the present study has low Cu abundances and Cu/Zr ratios that can be interpreted as due to equilibrium with sulfides (Figs. 3A and 4).

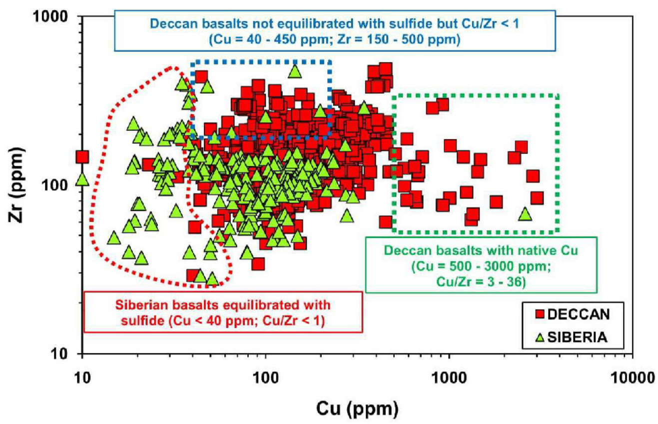

Fig. 4. Zr (ppm) *vs.* Cu (ppm) variation in the Deccan and Siberian continental flood basalts. Siberian basalts equilibrated with sulfide contain Cu < 40 ppm and Cu/Zr < 1. Note that low Cu/Zr ratio in the Deccan basalts is due higher Zr contents. High copper abundance in some of the Deccan basalts is due to presence of native copper. For discussion, see the text.

Further Si/Cu ratio is used to distinguish between silicate and sulfide fractionation (Fig. 5). During basaltic magma differentiation silica behaves less incompatibly than copper, therefore Si/Cu ratio slightly decreases during silicate-only fractionation. However, if sulfide minerals crystallize then copper becomes compatible and the Si/Cu ratio increases with magma evolution. The Deccan basalts show trends suggested by silicate-only fractionation whereas the Siberian basalts show variations that require sulfide minerals in the fractionation assemblage (Fig. 5). The Si/Cu ratio reaffirms the conclusions drawn from the other geochemical proxies that the Deccan basalts did not witness any major copper-sulfide formation event.

Vanadium is considered as an indicator of oxidation state of magma as V content in the magma is directly proportional to oxygen fugacity (fO_2) conditions (*see* Laubier et al., 2014 and references therein). The V occurs as V^{3+} and V^{4+} (Caniel, 1999; Gaetani and Grove, 1997) in the silicate magmas. Since V^{3+} preferentially enters crystal lattices of igneous minerals, with increasing fO_2 more of vanadium occurs as incompatible V^{4+} form (Laubier et al., 2014). Incompatibility of V increases with increasing fO_2 and becomes compatible with decreasing fO_2. V changes from compatible to incompatible element as oxygen fugacity changes from FMQ-1 to FMQ+1 (Laubier et al., 2014). V and Yb show similar partition behavior during crustal processes at constant fO_2 conditions (Laubier et al., 2014). However, Yb is a lithophile incompatible element in silicate magmas of basaltic composition and is not affected by fO_2 and fS_2 conditions (Farley, 1994) as a result sulfide segregation leads to lower V/Yb ratios in the associated basalts (Song et al., 2003). Therefore, V/Yb behavior during magma differentiation indirectly reflects varying fO_2 conditions. The V/Yb ratio would be higher for magmas differentiating at $fO_2 \geq$ FMQ

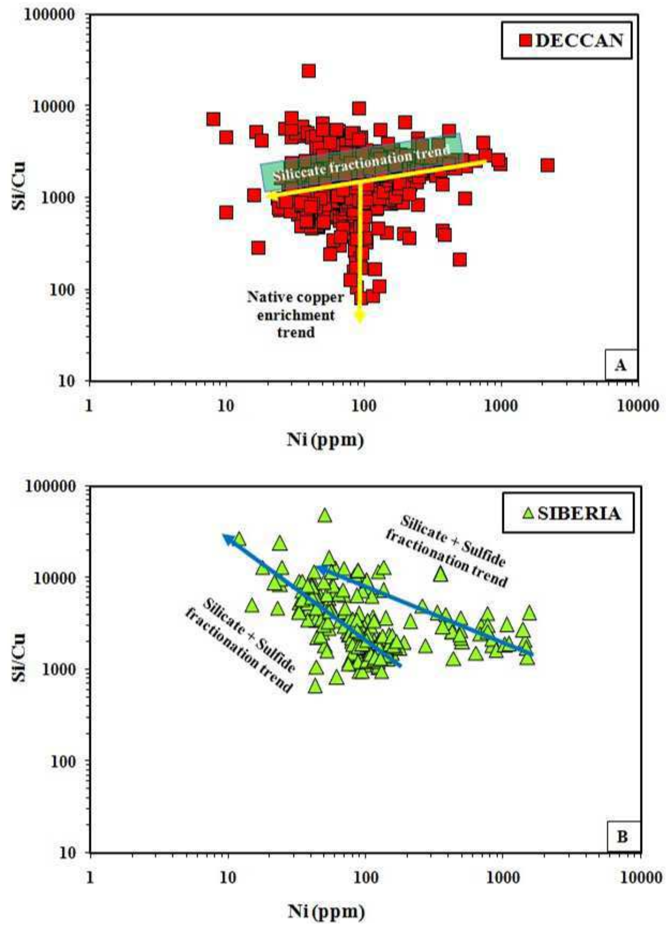

Fig. 5. Si/Cu *vs.* Ni (ppm) variations in the Deccan (**A**) and Siberian (**B**) continental flood basalts. Note distinctly different variation trends in the Deccan and Siberian basalts.

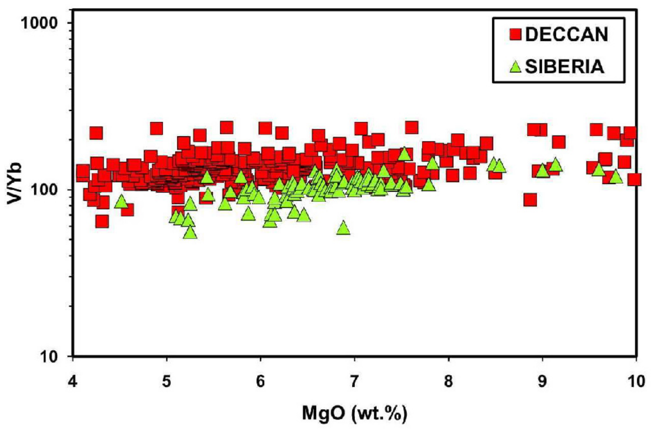

Fig. 6. V/Yb *vs.* MgO (wt.%) variation in the Deccan and Siberian continental flood basalts. Note higher V/Yb ratios in the Deccan compared to Siberian basalts. V/Yb ratio is very sensitive to fO_2 conditions. Sample with highly dispersed vanadium data (<5% samples) are not shown in the figure. For discussion, see the text.

and lower for magmas differentiating at fO_2<FMQ. The V/Yb ratios in the Siberian basalts are distinctly lower that in Deccan basalts at any given MgO content (Fig. 6). Based on V/Yb variation and comparison with the experimental results (see Fig. 3B in Laubier et al., 2014) we can infer that $fO_2$was higher in Deccan basalts than in Siberian basalts (Fig. 6). Lower fO_2 led to saturation of sulfur in the melt and its eventual separation as immiscible liquid fraction in the Siberian basalts. In contrast, higher fO_2 kept the Deccan magmas S-undersaturated in spite of higher absolute abundance of sulfur (see Keays and Lightfoot, 2010). It is suggested that the Deccan basalts fractionated under ≥FMQ conditions whereas the Siberian basalts fractionated under fO_2 conditions <FMQ. This variable fO_2 conditions subsequently controlled behavior of copper in the basaltic magma. The Deccan basalts have higher V/Yb ratios than the Siberian basalts at any given alkali content, especially at higher alkali abundances. In the Deccan basalts alkalies have increased with contamination. Higher V/Yb ratios at higher alkali contents, therefore, suggest that fO_2 might have actually increased with crustal contamination within the Deccan basalts. Whereas in the Siberian basalts a negative correlation between alkalies and V/Yb suggests that fO_2 decreased with contamination. The Deccan basalts were contaminated by granitic crust whereas the Siberian basalts were contaminated by sulfur-rich anhydrite and gypsum beds. The variable behaviour of V/Yb ratio in the Deccan and Siberian basalts reflects these variable contaminants. Although, locally the Deccan basalts may have fO_2 conditions <FMQ (Sen, 1986), based on V behavior (Fig. 6) it is inferred that on a regional scale the Deccan basalts indeed fractionated at $fO_2 \geq$ FMQ.

SULFIDE UNDERSATURATION IN THE DECCAN BASALTS

The behavior of copper in magmatic systems is influenced by S as sulfide (S^{-2}) and sulfide saturation primarily controls the genesis of chalcophile deposits (Imai et al., 1993; Sillitoe, 1997). Sulfur dissolution in the basaltic magma is directly proportional to temperature and iron content, and inversely proportional to pressure, fO_2, silica and alkali contents (see reviews by Carroll and Webster, 1994; Naldrett, 2004). The eruption temperatures of Deccan magmas are >1100°C (Gangopadhyay, 2003; Vijaya Kumar et al., 2010); at these high temperature sulfur will be in dissolved state (Haughton and Roeder, 1974; Naldrett, 2004). Rate of eruption of Deccan magma is also high (Courtillot et al., 1986), which may have resulted in a minimal decrease in temperature for a large decrease in pressure. The Deccan basaltic melt would have become S-undersaturated as adiabatic ascent of the magma would shift the magmas into the field of sulfur undersaturation (Mavrogenes and O'Neill, 1999).

It has been well established that the Deccan basalts contain higher FeO contents compared to other CFBs (Sen et al., 2001). The Fe-rich Deccan magmas are thus capable of dissolving much higher quantities of sulfur thereby restricting the immiscible separation of sulfide ore minerals. Based on V behavior (see earlier section) it is argued that on a regional scale the Deccan basalts indeed fractionated at fO_2≥FMQ thereby increasing their S dissolving capacity.

In Fig.7, copper variation in different formations of the Deccan volcanic province (DVP) is shown. Bushe and Poladpur formations contain most contaminated basalts in the DVP, therefore they are supposedly potential hosts for the immiscible sulfide deposits. However, ranges and averages of copper abundances in the Bushe and Poladpur formations are not distinctly different from other formations (Fig. 7). The Bushe and Poladpur formations are undepleted in copper (Av. Cu >100 ppm; Fig. 7; Keays and Lightfoot, 2010). Although the Bushe formation has lower copper abundances than the least contaminated Ambenali and Mahabaleshwar formations, it is not different from Jawahar-Igatpuri and Thakurwadi formations in terms of copper abundances (Fig. 7). The copper variation in different formations of the DVP does not indicate large scale sulfur saturation. The sulfur capacity of Deccan basalts ranges from 1130 ppm for Fe-poor Bushe basalts to 2390 ppm for Fe-rich Mahabaleshwar basalts (Keays and Lightfoot, 2010). In spite of large scale crustal contamination, the Deccan basalts did not achieve sulfur saturation (Keays and Lightfoot, 2010). Contamination by the granitic crust, which has lower S solubility than in the basaltic magmas did not lead to increase in sulfur in the contaminated Deccan basalts (Keays and Lightfoot, 2010; see section below). Even the extremely contaminated Bushe magmas were close to sulfur saturation but were not sulfide saturated (Keays and Lightfoot, 2010). The parental magmas to the Deccan basalts are considered to be S-undersaturated at mantle depths and remained S-undersaturated during magma differentiation and moderate to pronounced crustal contamination (Keays and Lightfoot, 2010). Based on copper evolution trends and geochemical proxies it is surmised that the Deccan basaltic magmas were not equilibrated with sulfide at any stage of their evolution.

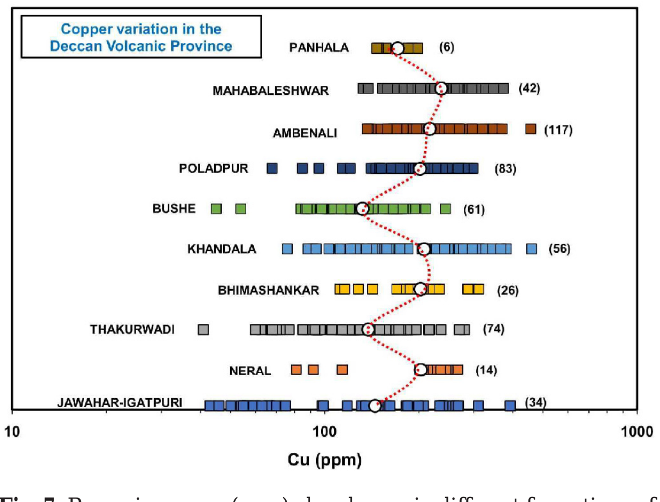

Fig. 7. Range in copper (ppm) abundances in different formations of the Deccan volcanic province. Variations in the average copper concentrations with stratigraphy are also shown. Numbers in parenthesis indicate number of basalt samples compiled from each formation.

SOURCE *VERSUS* PROCESS CONTROL ON COPPER SULFIDE MINERALIZATION

The relative control of mantle source *versus* emplacement and differentiation processes on the Cu-sulfide mineralization in the CFBs is hotly debated (Arndt et al., 2005; Zhang et al., 2008). Zhang et al. (2008) suggested that there are fundamental differences in the CFBs as controlled by the composition and structure of old lithospheric roots. It has been argued that the lithosphere plays a significant role in the formation of large copper deposits. If the plume-lithosphere interaction is minimal, then those provinces are unlikely to contain the chalcophile deposits. Zhang et al. (2008) argue that the CFBs are born unequal in terms of their ore potential. However, there are many others who argue that magma differentiation and crustal contamination are significant to the ore genesis within the CFBs (Lightfoot et al., 1994; Naldrett, 1992 and 1999; Naldrett et al., 1992 and 1996; Lesher and Campbell, 1993; Ripley et al., 2002; Arndt et al., 2005; Lightfoot and Keays, 2005; Wilson and Churnett, 2006; Keays and Lightfoot, 2007; Keays and Lightfoot, 2010). Plume-derived flood basaltic provinces of Siberia, West Greenland and Deccan show distinctly different potentials for sulfide mineralization. The Siberian basalts contain giant Cu-Ni-PGE deposits (Naldrett, 1999 and 2010), whereas the West Greenland flood basalts contain only small deposits of nickel sulfide (Keays and Lightfoot, 2007) and Deccan is more or less barren with respect to sulfide mineralization (Keays and Lightfoot, 2010; present study). Chalcophile element depletion with progressive crustal contamination is characteristically represented in Siberian and Greenland flood basalt provinces (Keays and Lightfoot, 2007). Separation of immiscible sulfide droplets and consequent chalcophile depletion in the silicate magmas could be at deeper levels as in Siberia or at shallower level as in Greenland (Keays and Lightfoot, 2007).

It is tested here the relative contribution of *source* (mantle) versus *process* (differentiation) on copper abundances in the Deccan basalts. In a recent study, Vijaya Kumar et al. (2018) have demarcated Deccan basalts into Type I and Type II categories with distinct trace element and isotope characteristics. Type I Deccan basalts with Th/Ta ratios <2.4 are exclusively derived from the asthenosphere/plume sources (Fig. 8A). The absence of basalts with typical MORB signatures in the Deccan volcanic province is affirmed by Zr/Nb and Th/Ta relationship (Fig. 8A). The Type II Deccan basalts with Th/Ta ratios >4.6 display sub-continental lithosphere mantle signatures (Fig. 8A). The Type I and Type II Deccan basalts with Th/Ta ratios between 2.4 and 4.6 suggest asthenosphere/plume and lithosphere interaction (Vijaya Kumar et al., 2018). The geochemical diversity in the DVP seems to be an outcome of contributions from both sub-lithospheric (plume/asthenosphere) and sub-continental lithospheric mantle sources. It has been suggested that most of the chalcophile elements in the continental flood basalts were scavenged from sub-continental lithosphere mantle (Zhang et al., 2008; Griffin et al., 2013) by the asthenosphere-derived melts. To test this hypothesis, we have compared the copper abundances of the Type I and Type II basalts, which are derived from asthenosphere/plume and sub-continental lithosphere respectively (Fig. 8B). Both the Type I and Type II basalts with distinct Th/Ta ratios have very similar copper abundances suggesting that asthenosphere/plume and sub-continental lithosphere have contributed comparable amounts of chalcophile elements to the continental flood basalts. Therefore, it is argued that the formation or non-formation of copper sulfide deposits in the continental flood basalt provinces is controlled by sulfur saturation of the magma at crustal depths. The crustal processes of fractionation and assimilation of sulfur-rich sediments seems to play dominant role in the sulfur-saturation of the magmas consequently the formation of copper sulfide deposits (Keays and Lightfoot, 2010).

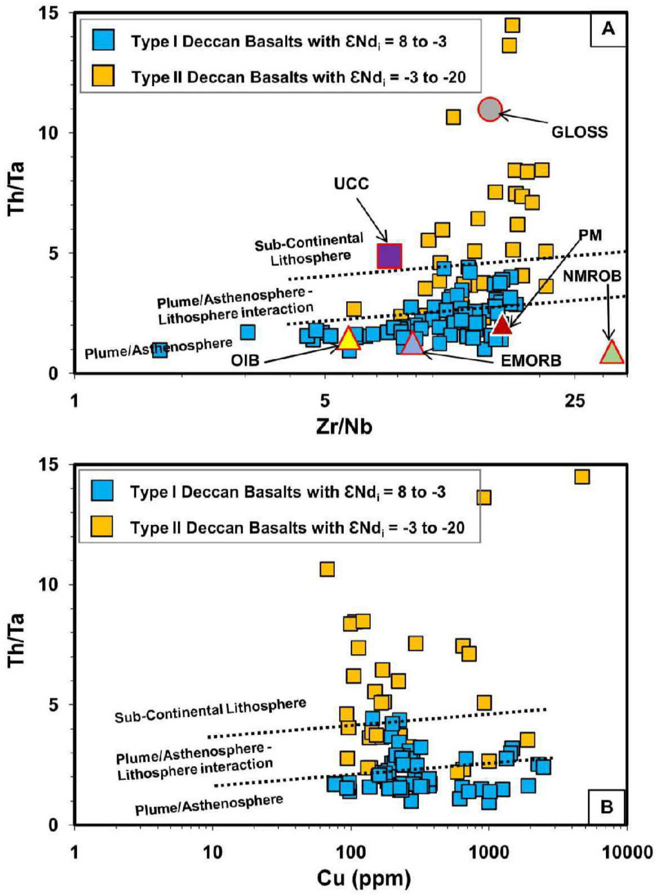

Fig. 8. Th/Ta *vs.* Zr/Nb (**A**) variations show two types of sources (Plume/Asthenosphere and Sub-Continental Lithospheric Mantle) for the Deccan basalts. Th/Ta *vs.* Cu (ppm) plot (**B**) illustrates Cu variations with respect to different sources in the Deccan basalts. **PM** (Primitive Mantle; Th = 0.085 ppm; Nb = 0.713 ppm; Zr = 11.2 ppm; Ta = 0.041 ppm), **N-MORB** (Normal Mid-Ocean Ridge Basalt; Th = 0.12 ppm; Nb = 2.33 ppm; Zr = 74 ppm; Ta = 0.132 ppm), **E-MORB** (Enriched Mid-Ocean Ridge Basalt; Th = 0.6 ppm; Nb = 8.3 ppm; Zr = 73 ppm; Ta = 0.47 ppm), **OIB** (Ocean Island Basalt; Th = 4 ppm; Nb = 48 ppm; Zr = 73 ppm; Ta = 2.7 ppm), **UCC** (Upper Continental Crust; Th = 10.7 ppm; Nb = 25 ppm; Zr = 190 ppm; Ta = 2.2 ppm) and **GLOSS** (Th = 6.91 ppm; Nb = 8.94; Zr = 280 ppm; Ta = 0.63 ppm) compositions are after Sun and McDonough (1989), Plank and Langmuir (1998) and Rudnick and Gao (2003).

If crustal contamination of the sulfur-rich sediments is the main mechanism of copper sulfide deposit formation then the sulfide deposits should form in the most contaminated basalts. Since copper would be removed in the sulfide deposits then the associated contaminated basalts will have lower copper abundances. $(La/Lu)_N$ ratios and neodymium isotopes are good monitors of crustal contamination. Higher $(La/Lu)_N$ ratios are prominent in some of the Deccan basalts with positive εNd_i values (Fig. 9; Vijaya Kumar et al., 2018). This could be due to lower degrees of melting of the sub-lithospheric mantle within the garnet stability field (Vijaya Kumar et al., 2018). The $(La/Lu)_N$ ratios continuously increase with progressive crustal contamination or assimilation fractional crystallization. If sulfur-saturation increases with progressive assimilation, resulting in the removal of copper in the sulfide deposits, then a negative correlation between $(La/Lu)_N$ ratios and copper abundance is expected. This predicted relationship is conspicuously shown by the Siberian basalts (Fig. 9). The basalts with high $(La/Lu)_N$ ratios have lower copper

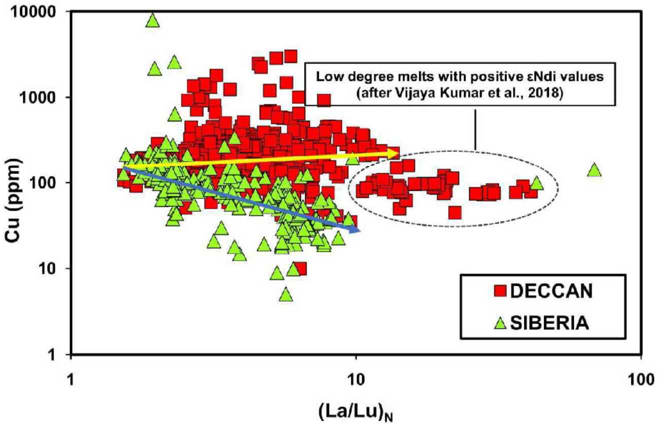

Fig. 9. Cu (ppm) *vs.* $(La/Lu)_N$ (where N in the subscript indicates Chondrite normalized) variations in Deccan and Siberian continental flood basalts. Note distinctly different variation trends for Cu with increasing $(La/Lu)_N$ ratios in the Deccan and Siberian basalts. Chondrite normalizing values are after Hanson (1980).

concentrations indicating the removal of copper in the associated sulfide deposits. Whereas the Deccan basalts show flat to slightly increasing trend for copper with increasing $(La/Lu)_N$ ratios (Fig. 9) thereby suggesting that copper *was not removed* from the silicate magma.

Age-corrected epsilon neodymium (εNd_i) becomes increasingly negative with progressive crustal contamination. If the basalts with negative εNd_i contain very low copper abundances –a positive εNd_i-Cu correlation–then it suggests the possibility of presence of copper sulfide deposits. However, if the copper abundances do not decrease in the negative εNd_i basalts then the possibility of presence of copper deposits could be meager. The Deccan basalts for a large variation in the εNd_i (+8 to -15) values show almost a flat trend for copper (Fig. 10A). Whereas the Siberian basalts, with world-class copper deposits, depict the predicted positive εNd_i-Cu relationship (Fig. 10B). Samples with low εNd_i values show depletion in chalcophile elements (Fig. 10B; Naldrett et al., 1992; Arndt et al., 2003). In spite of large scale crustal contamination, the Deccan basalts did not achieve sulfur saturation (Keays and Lightfoot, 2010; this study). Although assimilation of granitic material decreases FeO content of the hybrid magma it may not be sufficient to initiate sulfur saturation as granite has less S than that of basalt and conspicuously illustrated by the Deccan basalts (Keays and Lightfoot, 2010). This relationship once again reiterates that copper in the DVP resided in the silicate magma but was not partitioned into immiscible sulfides. To test the hypothesis, one flood basalt province without Cu-sulfide mineralization (Fig. 10C; Etendeka) and one flood basalt province with Cu-sulfide mineralization is included (Fig. 10D; Emeishan). The Cu-εNd_i relationships in Etendeka and Emeishan flood basalt provinces support the predicted model.

GEOCHEMICAL PROXIES FOR COPPER SULFIDE MINERALIZATION IN THE CFBs: SOME SPECULATIONS

Chalcophile depletion in erupted flood basalts has been utilized as an important exploration tool for sulfide deposits in coeval sub-

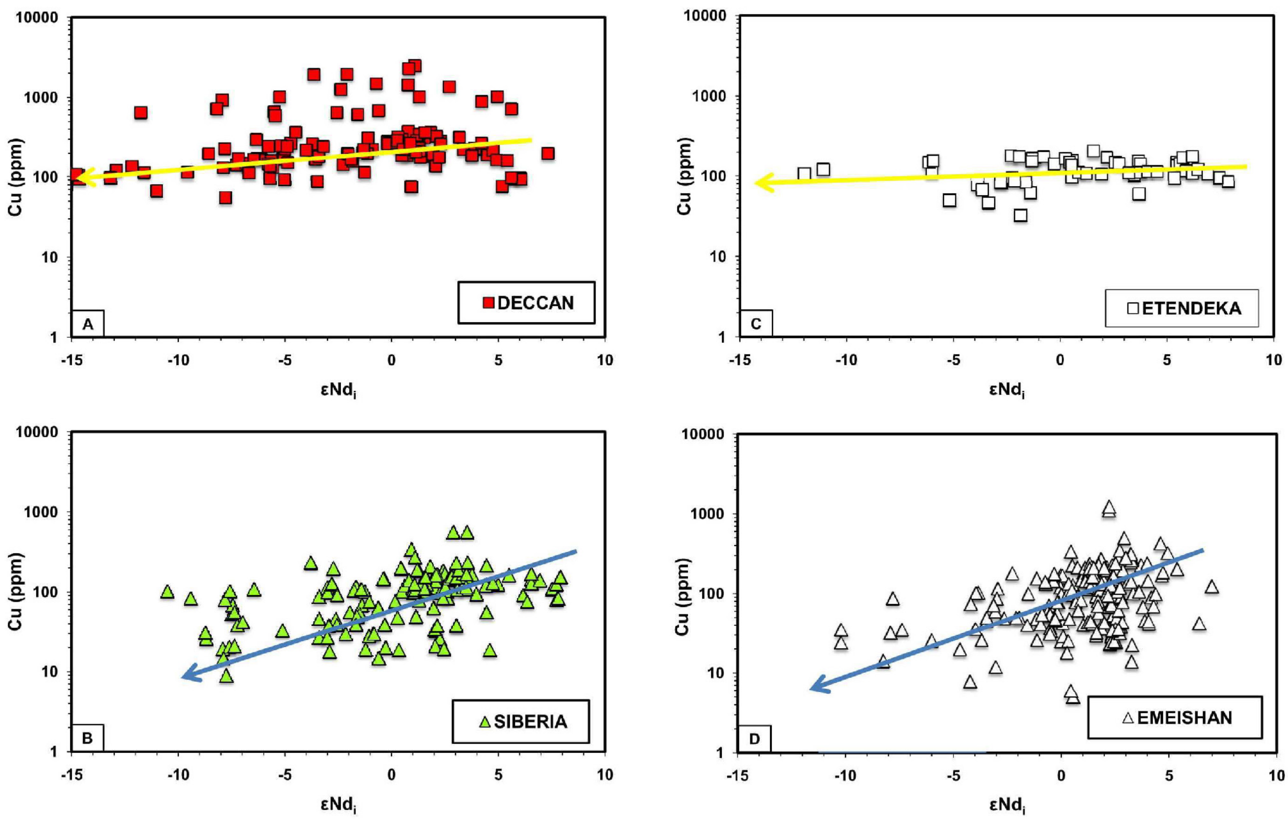

Fig. 10. Cu (ppm) *vs.* εNd_i variations in Deccan (**A**) and Siberian (**B**) continental flood basalts. Note distinctly different variation trends for Cu with increasing contamination (i.e. decreasing εNd_i values) in the Deccan and Siberian basalts. We interpret that the Deccan trend typifies possible absence of large scale Cu-sulfide mineralization whereas the Siberian trend indicates possible presence large scale Cu-sulfide deposits. To test our hypothesis, we have included one flood basalt province without Cu-sulfide mineralization (C; Etendeka) and one flood basalt province with Cu-sulfide deposit (D; Emeishan). The Cu-εNd_i relationships in Etendeka and Emeishan support our predicted model. Data for Etendeka and Emeishan basalts was extracted from GEOROC data files.

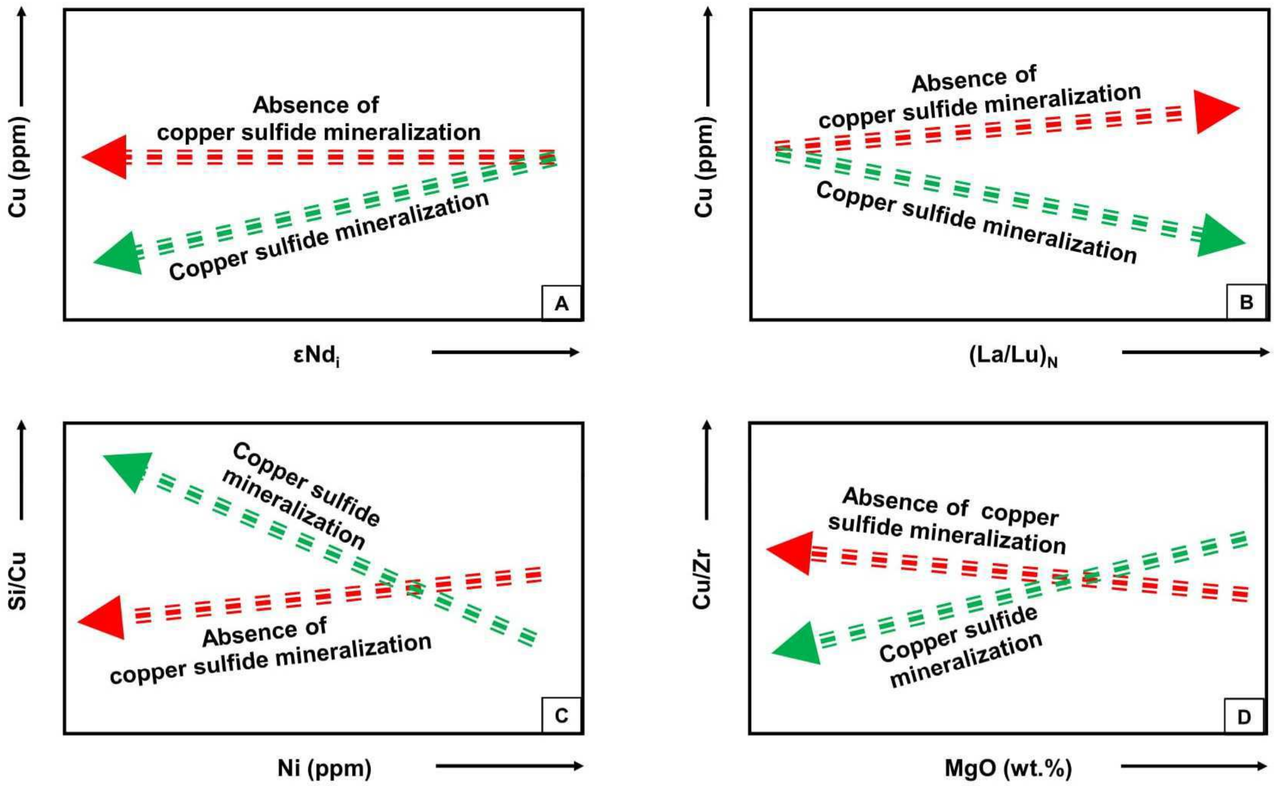

Fig. 11. Schematic binary variation plots, Cu (ppm) *vs.* εNd_i (**A**); Cu (ppm) *vs.* $(La/Lu)_N$ (**B**); Si/Cu *vs.* Ni (ppm) (**C**); Cu/Zr *vs.* MgO (wt.%) (**D**), illustrating the geochemical trends for possible presence or absence of Cu-sulfide deposits in the continental flood basalt provinces.

volcanic intrusions (Naldrett, 1992; Naldrett and Lightfoot, 1999; Li et al., 2009). Based on distinct variations in the Cu-sulfide deposit-bearing Siberian basalts and Cu-sulfide deposit-absent Deccan basalts, we propose general geochemical signatures (Fig. 11) that can be tested as preliminary exploration tools for copper mineralization in the continental flood basalt provinces. If copper abundances remain constant or decrease slightly with decreasing εNd_i values then the possibility of CFBs containing Cu-sulfide deposits is minimal (Fig. 11A). If there is a drastic decrease in copper concentrations with decreasing εNdi values then the possibility of CFBs containing Cu-sulfide deposits is robust (Fig. 11A). A similar relationship between $(La/Lu)_N$ and Cu (Fig. 11B) can be tested to distinguish Cu-sulfide deposit-bearing and non-bearing CFBs. A strong increasing trend for Si/Cu with decreasing Ni (Fig. 11C) suggests the possibility of Cu-sulfide mineralization but a decreasing trend for Si/Cu suggests possible absence of Cu-sulfide mineralization (Fig. 11C). An increase in Cu/Zr ratio with decreasing MgO suggests that the sulfide was not saturated and there is no silicate-sulfide segregation (Fig. 11D). Sulfide saturation and eventual separation results in decreasing Cu/Zr with magma evolution (Fig. 11D).

THE WAY FORWARD

Cu is chalcophile in all crystallizing environments (Greaney et al., 2017) and mostly partition into sulfides, although small amounts of these metals can be incorporated in silicate and oxide minerals and may also occur in native state (Seward, 1971; Gaetani and Grove, 1997; Hart and Dunn, 1993; Stanton, 1994). However, this variable distribution is strongly controlled by sulfur-saturation and segregation. It is evident that the sulfur-saturation was not attained in the DVP; hence, possibility of the DVP hosting large-scale Cu-sulfide deposits is meager. Which leaves us with a question whether the DVP does not contain copper deposits of any form or it is only sulfide that could be absent. We argue that the DVP could be a potential source for native copper deposits. In the absence of sulfide saturation, 1/3 of copper could be present in silicates and oxides and 2/3 in native state (Cornwall, 1956). Cu in Fe-Ti oxide could be around 300 ppm; 600 to 24,000 ppm in hematite and pseudobrookite and ~250 ppm in pyroxenes (Jensen, 1982). Copper concentrated in opaque oxides and pyroxenes may get released during oxidation during subaerial weathering (Jensen, 1982; LeHuray, 1989).

There are many examples of native copper associated with flood basalts (Cornwall, 1956); some are at a deposit scale (Brown, 2006; Wang et al, 2006; Pinto et al., 2011). The average copper content in Deccan basalts (>200 ppm) is much higher than the average copper content in Parana basalts (152 ppm; Crockett, 2002), which contains known native copper deposits (Pinto et al., 2011). Several occurrences of native Cu were reported from different parts of the DVP (Bombay-Saurashtra regions in northern Deccan province; Roy, 1953; Dunn and Jhingran, 1965; Radhakrishna and Pandit, 1973; Alexander and Thomas, 2011). Native copper in Deccan basalts is associated with clay minerals, zeolites, quartz and calcite (Roy, 1953; Radhakrishna and Pandit, 1973; Alexander and Thomas, 2011) similar to native copper deposits elsewhere (Cornwall, 1956; Pinto et al., 2011).

In addition to native copper, many hydrothermal Cu-sulfide occurrences are also known from the DVP (Alexander and Thomas, 2011; Randive, 2015, *pers. Comm.*). Native copper or late stage Cu-sulfide in basalts may directly crystallize as the lava flow solidified or form by epigenetic hydrothermal fillings. Epigenetic native copper deposits are widespread in Parana basaltic province (Pinto et al., 2011). The physical conditions of native copper formation in the Deccan (<200°C; Roy, 1953) and Parana (100-150°C; Pinto et al., 2011) and mineralogical associations are similar suggesting that Deccan native copper formation also could be due to hydrothermal epigenetic origin. All the geochemical evidences point to absence of Cu-sulfide mineralization in the DVP. However, there are positive chances of native copper deposits in the DVP. Large hydrothermal systems should be the prime targets for the native copper mineralization in the DVP. The focus should be on *what to search for* in addition to *where to search*.

CONCLUSIONS

In the present study the possibility of Cu-sulfide mineralization in the ~ 65 Ma Deccan volcanic province (DVP), India is explored. The Siberian and Deccan volcanic provinces have been considered to constrain the mechanism of Cu-sulfide ore formation in the continental flood basalt provinces. Based on the behavior of copper and other geochemical proxies (including Cu/Zr, Si/Cu, V/Yb and εNd_i) we suggest that the Deccan magmas were not equilibrated with sulfide at any stage of their evolution. Lower Cu/Zr in some of the Deccan basalts is possibly due to higher Zr contents in the basalts rather than lower Cu abundances due to silicate-sulfide magma equilibrium. Nevertheless, the geochemical behavior of copper in the Deccan basalts suggests that there are positive chances for native copper deposits in the DVP. It is suggested that the Cu-sulfide mineralization in the CFBs is magma evolution process-controlled rather than mantle source-controlled. We also infer that Cu/Zr, Si/Cu and V/Yb ratios and εNd_i–Cu relationships in the erupted basalts indicate sulfide saturation or otherwise at any stage of magma evolution and thus can be utilized as preliminary exploration tools for Cu-sulfide mineralization in the CFBs.

Acknowledgements: This work is partially funded by UGC-SAP of the School of Earth Sciences and DST-INSPIRE (JRF (IF160420) to MBL). Pritam, Zubair and Jafar helped in compiling the geochemical data. An anonymous Journal reviewer provided critical and constructive comments on an earlier version of manuscript. Geochemical data used in this paper were mainly extracted from the GEOROC database maintained by the Max Planck Institute für Chemie in Mainz, Germany (http://georoc.mpch-mainz.gwdg.de/georoc/). We thank all the above-mentioned people and institutions for their help and support.

References

Alexander, P.O. and Thomas, H. (2011) Copper in Deccan basalts (India): review of the abundance and patterns of distribution. Bol. Inst. Fisio. Geol., v.79–81, pp.107–112.

Allegre, C.J., Birck, J.L., Capmas, F. and Courtillot, V. (1999) Age of the Deccan traps using ^{187}Re–^{187}Os systematics. Earth Planet. Sci. Lett., v.170, pp.197–204.

Arndt, N., Lesher, C.M. and Czamanske, G.K. (2005) Mantle-derived magmas and magmatic Ni-Cu-(PGE) deposits. Econ. Geol., 100th Anniversary volume, pp.5–24.

Arndt, N.T., Czamanske, G.K., Walker, R.J., Chauvel, C. and Fedorenko, V.A. (2003) Geochemistry and origin of the intrusive hosts of the Noril'sk-Talnakh Cu-Ni-PGE sulfide deposits. Econ. Geol., v.98, pp.495–515.

Baksi, A.K. (1994) Geochronological studies on whole-rock basalts, Deccan Traps, India: evaluation of the timing of volcanism relative to the KT boundary. Earth Planet. Sci. Lett., v.121, pp.43–56.

Barnes, S.J. and Lightfoot, P.C. (2005) Formation of magmatic nickel sulfide ore deposits and processes affecting their copper and platinum-group contents. Econ. Geol., 100th Anniversary volume, pp.173–213.

Beane, J.E., Turner, C.A., Hooper, P.R., Subbarao, K.V. and Walsh, J.N. (1986) Stratigraphy, composition and form of the Deccan basalts, Western Ghats, India. Bull. Volcanol., v.48, pp.61–83.

Brown, A.C. (2006) Genesis of native copper lodes in the Keweenaw District, northern Michigan: a hybrid evolved meteoric and metamorphogenic model. Econ. Geol., v.101, pp.1437–1444.

Brügmann, G.E., Naldrett, A.J., Asif, M., Lightfoot, P.C., Gorbachev, N.S. and Fedorenko, V.A. (1993) Siderophile and chalcophile metals as tracers of the evolution of the Siberian Trap in the Noril'sk region, Russia. Geochim. Cosmochim. Acta, v.57, pp.2001–2018.

Buchanan, D.L. and Nolan, J. (1979) Solubility of sulfur and sulfide immiscibility in synthetic tholeiitic melts and their relevance to Bushveld Complex rocks. Canadian Mineral., v.17, pp.483–494.

Campbell, I.H., Czamanske, G.K., Fedoernko, V.A., Hill, R.I., Stepanov, V.A. and Kunilov, V.E. (1992) Synchronism of the Siberian traps and the Permian-Triassic boundary. Science, v.258, pp.1760–1763.

Canil, D. 1999. Vanadium partitioning between orthopyroxene, spinel and silicate melt and the redox state of mantle source regions for primary magmas. Geochim. Cosmochim. Acta, v.63, pp.557–572.

Carroll, M.R. and Rutherford, M.J. (1987) The stability of igneous anhydrite—experimental results and implications for sulfur behavior in the 1982 El Chichon trachyandesite and other evolved magmas. Jour. Petrol., v.28, pp.781–801.

Carroll, M.R. and Webster, J.D. (1994) Solubilities of sulfur, noble gases, nitrogen, chlorine, and fluorine in magmas, *In:* M.R. Carroll and J.R. Holloway (Ed.), Volatiles in Magmas: Reviews in Mineralogy, v.30, pp.231–279.

Chakrabarti, R. and Basu, A.R. (2006) Trace element and isotopic evidence for Archean basement in the Lonar crater impact breccias, Deccan Volcanic Province. Earth Planet. Sci. Lett., v.247, pp.197–211.

Cornwall, H.R. (1956) A summary of ideas on the origin of native copper deposits. Econ. Geol., v.51, pp.615–631.

Courtillot, V., Besse, J., Vandamme, D., Montigny, R., Jaeger, J.J. and Cappetta, H. (1986) Deccan flood basalts at the Cretaceous/Tertiary boundary? Earth Planet. Sci. Lett., v.80, pp.361–374.

Courtillot, V., Davaille, A., Besse, J. and Stock, J. (2003) Three distinct types of hotspots in the Earth's mantle. Earth Planet. Sci. Lett., v.205, pp.295–308.

Crocket, J.H. (2002) Platinum-group element geochemistry of mafic and ultramafic rocks. *In:* L.J. Cabri (Ed.), The geology, geochemistry, mineralogy, and mineral beneficiation of platinum-group elements: London, Ontario, Canada, Canadian Inst. Mining Metal. Petrol, v.54, pp.177–210.

Czamanske, G.K., Wooden, J.L., Zientek, M.L., Fedorenko, V.A., Zen'ko, T.E., Kent, J., King, B.S.W., Knight, R.J. and Siems, D.F. (1994) Geochemical and isotopic constraints on the petrogenesis of the Noril'sk-Talnakh ore-forming system. Ont. Geol. Surv. Spec. Publ., v.5, pp.313–342.

Duncan, R.A. and Pyle, D.G. (1988) Rapid eruption of the Deccan flood basalts, western India. Nature, v.333, pp.841–843.

Dunn, J.A. and Jhingran, A.G. (1965) "Copper". Bull. Geol. Surv. India, Econ. Geol., v.23, pp.1–204.

Farley, K.N. (1994) Oxidation state and sulfur concentrations in Lau Basin basalts. *In:* Proc. ODP, Sci. Results, TX (Ocean Drilling Program), v.135, pp.603–613.

Fedorenko, V.A. (1994) Evolution of magmatism as reflected in the volcanic sequence of the Noril'sk region. *In:* P.C. Lightfoot and A.J. Naldrett. (Ed.), The Sudbury-Noril'sk Symposium. Special Volume Ont. Geol. Surv., v.5, pp.171–183.

Gaetani, G.A. and Grove, T.L. (1997) Partitioning of moderately siderophile elements among olivine, silicate melt, and sulfide melt: constraints on core formation in the Earth and Mars. Geochim. Cosmochim. Acta, v.61, pp.1829–1846.

Gangopadhyay, A., Sen, G. and Keshav, S. (2003) Experimental crystallization of Deccan basalts at low pressure: effect of contamination on phase equilibrium. Indian Jour. Geol., v.75, pp.54-71.

Greaney, A.T., Rudnick, R.L., Helz, R.T., Gaschnig, R.M., Piccoli, P.M. and Ash, R.D. (2017) The behavior of chalcophile elements during magmatic differentiation as observed in Kilauea Iki lava lake, Hawaii. Geochim. Cosmochim. Acta, v.210, pp.71–96.

Griffin, W.L., Begg, G.C. and O'reilly, S.Y. (2013) Continental-root control on the genesis of magmatic ore deposits. Nature Geoscience, v.6, pp.905–910.

Hanson, G.N. (1980) Rare earth elements in petrogenetic studies of igneous systems. Ann. Rev. Earth Planet. Sci., v.8, pp.371–406.

Hart, S.R. and Dunn, T. (1993) Experimental cpx/melt partitioning of 24 trace elements. Contrib. Mineral. Petrol., v.113, pp.1–8.

Haughton, D.R., Roeder, P.L. and Skinner, B.J. (1974) Solubility of sulfur in mafic magmas. Econ. Geol., v.69, pp.451–467.

Hawkesworth, C.J., Lightfoot, P.C., Fedorenko, V.A., Blake, S., Naldrett, A.J., Doherty, W. and Gorbachev, N.S. (1995) Magma differentiation and mineralisation in the Siberian continental flood basalts. Lithos, v.34, pp.61–88.

Imai, A., Listanco, E.L. and Fujii, T. (1993) Petrologic and sulfur isotopic significance of highly oxidized and sulfur-rich magma of Mt. Pinatubo, Philippines. Geology, v.21, pp.699–702.

Jay, A.E. and Widdowson, M. (2008) Stratigraphy, structure and volcanology of the SE Deccan continental flood basalt province: implications for eruptive extent and volumes. Jour. Geol. Soc. London, v.165, pp.177–188.

Jensen, A. (1982) The distribution of Cu across three basaltic lava flows from the Faeroe Islands. Bull. Geol. Soc. Denmark, v.31, pp.1–10.

Jerram, D.A. and Widdowson, M. (2005) The anatomy of Continental flood basalt provinces: geological constraints on the processes and products of flood volcanism. Lithos, v.79, pp.385–405.

Jugo, P.J. (2009) Sulfur content at sulfide saturation in oxidized magmas. Geology, v.37, pp.415–418.

Jugo, P.J., Luth, R.W. and Richards, J.P. (2005) Experimental data on the speciation of sulfur as a function of oxygen fugacity in basaltic melts. Geochim. Cosmochim. Acta, v.69, pp.497–503.

Keays, R.R. (1995) The role of komatiitic and picritic magmatism and S-saturation in the formation of ore deposits. Lithos, v.34, pp.1–18.

Keays, R.R. and Lightfoot, P.C. (2007) Siderophile and chalcophile metal variations in Tertiary picrites and basalts from West Greenland with implications for the sulphide saturation history of continental flood basalt magmas. Mineral. Deposita, v.42, pp.319–336.

Keays, R.R. and Lightfoot, P.C. (2010) Crustal sulfur is required to form magmatic Ni–Cu sulfide deposits: evidence from chalcophile element signatures of Siberian and Deccan Trap basalts. Mineral. Deposita, v.45, pp.241–257.

Krishnamurthy, P. (2015) Chalcophile element depletion in lower Deccan trap formations and implications for Cu-Ni-PGE sulphide mineralization in the Deccan Traps, India akin to those of Norilsk-Talnakh, Siberian traps, Russia. Jour. Geol. Soc. India, v.85, pp.411–418.

Krivolutskaya, N.A. (2011) Formation of PGM-Cu-Ni deposits in the process of evolution of flood-basalt magmatism in the Noril'sk region. Geol. Ore Deposits, v.53, pp.309-339.

Laubier, M., Grove, T.L. and Langmuir, C.H. (2014) Trace element mineral/melt partitioning for basaltic and basaltic andesitic melts: an experimental and laser ICP-MS study with application to the oxidation state of mantle source regions. Earth Planet. Sci. Lett., v.392, pp.265–278.

Lee, C.T.A., Luffi, P., Chin, E.J., Bouchet, R., Dasgupta, R., Morton, D.M., Le Roux, V., Yin, Q.Z. and Jin, D. (2012) Copper systematics in arc magmas and implications for crust-mantle differentiation. Science, v.336, pp.64–68.

LeHuray, A.P. (1989) Native copper in ODP Site 642 tholeiites. *In:* O. Eldholm, J. Thiede, E. Taylor, et al. (Eds.), Proc. ODP, Sci. Results, College Station, TX (Ocean Drilling Program), v.104, pp. 411–417.

Lesher, C.M. and Campbell, I.H. (1993) Geochemical and fluid dynamic modeling of compositional variations in Archean komatiite-hosted nickel sulfide ores in Western Australia. Econ. Geol., v.88, pp.804–816.

Lesher, C.M., Lee, R.F., Groves, D.I., Bickle, M.J. and Donaldson, M.J. (1981) Geochemistry of komatiites from Kambalda, Western Australia: 1. Chalcophile element depletion—a consequence of sulfide liquid separation from komatiitic magmas. Econ. Geol., v.76, pp.1714–1728.

Li, C. and Naldrett, A.J. (1999) Geology and petrology of the Voisey's Bay intrusion: reaction of olivine with sulfide and silicate liquids. Lithos, v.47, pp.1–31.

Li, C., Ripley, E.M. and Naldrett, A.J. (2009) A new genetic model for the giant Ni-Cu-PGE sulfide deposits associated with the Siberian flood basalts. Econ. Geol., v.104, pp.291–301.

Lightfoot, P.C. and Keays, R.R. (2005) Siderophile and chalcophile metal variations in flood basalts from the Siberian trap, Noril'sk region. Implications for the origin of the Ni-Cu-PGE sulfide ores. Econ. Geol., v.100, pp.439–462.

Lightfoot, P.C., Hawkesworth, C.J., Hergt, J., Naldrett, A.J., Gorbachev, N.S. and Fedorenko, V.A. (1993) Remobilisation of the continental lithosphere by a mantle plume: major-, trace-element and Sr-, Nd-, and Pb-isotope evidence from picritic and tholeiitic lavas of the Noril'sk District, Siberian Trap, Russia. Contrib. Mineral. Petrol., v.114, pp.171–188.

Lightfoot, P.C., Naldrett, A.J., Gorbachev, N.S., Fedorenko, V.A., Hawkesworth, C.J., Hergt, J. and Doherty, W. (1994) Chemostratigraphy of Siberian trap lavas, Noril'sk District, Russia: implications for the source of flood basalt magmas and their associated Ni-Cu mineralization. Ont. Geol. Surv. Spec. Publ., v.5, pp.283–312.

Lightfoot, P.C., Naldrett, A.J., Gorbachev, N.S., Doherty, W. and Fedorenko, V.A. (1990) Geochemistry of the Siberian Trap of the Noril'sk area, USSR, with implications for the relative contributions of crust and mantle to flood basalt magmatism. Contrib. Mineral. Petrol., v.104, pp.631–644.

MacLean, W.H. (1969) Liquidus phase relations in the FeS-FeO-Fe_2O_3-SiO_2 system and their application in geology. Econ. Geol., v.64, pp.865–884.

Mahoney, J.J., Sheth, H.C., Chandrasekharam, D. and Peng, Z.X. (2000) Geochemistry of flood basalts of the Toranmal section, northern Deccan Traps, India: implications for regional Deccan stratigraphy. Jour. Petrol., v.41, pp.1099–1120.

Maier, W.D., Li, C. and De Waal, S.A. (2001) Why are there no major Ni–Cu sulfide deposits in large layered mafic-ultramafic intrusions? Canadian Mineral., v.39, pp.547–556.

Mavrogenes, J.A. and O'Neill, H.S.C. (1999) The relative effects of pressure temperature and oxygen fugacity on the solubility of sulfide in mafic magmas. Geochim. Cosmochim. Acta, v.63, pp.1173–1180.

Mungall, J.E., Hanley, J.J., Arndt, N.T. and Debecdelievre, A. (2006) Evidence from meimechites and other low-degree mantle melts for redox controls on mantle-crust fractionation of platinum-group elements. Proc. Natl. Acad. Sci. USA, v.103, pp.12695–12700.

Nadeau, O., Stix, J. and Williams-Jones, A.E. (2013) The behavior of Cu, Zn and Pb during magmatic–hydrothermal activity at Merapi volcano, Indonesia. Chem. Geol., v.342, pp.167–179.

Naldrett, A.J. (1992) A model for the Ni-Cu-PGE ores of the Noril'sk region and its application to other areas of flood basalt. Econ. Geol., v.87, pp.1945–1962.

Naldrett, A.J. (1999) World-class Ni-Cu-PGE deposits: key factors in their genesis. Mineral. Deposita, v.34, pp.227–240.

Naldrett, A.J. (2004) Magmatic Sulfide Deposits. Geology, Geochemistry, and Exploration, Springer, Berlin, 727pp.

Naldrett, A.J. (2010) Secular variation of magmatic sulfide deposits and their source magmas. Econ. Geol., v.105, pp.669–688.

Naldrett, A.J. and Lightfoot, P.C. (1993) A model for giant magmatic sulphide deposits associated with flood basalts. Soc. Econ. Geol. Spec. Publ. No. 2, pp.81–124

Naldrett, A.J. and Lightfoot, P.C. (1999) Ni–Cu–PGE deposits of the Noril'sk region, Siberia: their formation in conduits for flood basalt volcanism. *In*: R.R. Keays, C.M. Lesher, P.C. Lightfoot and C.E.G. Farrow (Eds.), Dynamic processes in magmatic ore deposits and their application in mineral exploration, Geol. Asso. Canada Short Course Notes, v.3, pp.195–250

Naldrett, A.J., Fedorenko, V.A., Lightfoot, P.C., Gorbachev, N.S., Doherty, W., Asif, M., Lin, S. and Johan, Z. (1995) A model for the formation of the Ni–Cu–PGE deposits of the Noril'sk region. Economic Geology in Europe and Beyond, British Geol. Surv., pp.18–36.

Naldrett, A.J., Fedorenko, V.A., Lightfoot, P.C., Kunilov, V.I., Gorbachev, N.S., Doherty, W. and Johan, Z. (1996) Controls on the composition of Ni-Cu sulfide deposits as illustrated by those at Noril'sk, Siberia. Econ. Geol., v.91, pp.751–773.

Naldrett, A.J., Lightfoot, P.C., Fedorenko, V.A., Doherty, W. and Gorbachev, N.S. (1992) Geology and geochemistry of intrusions and flood basalts of the Noril'sk region, USSR, with implication for the origin of the Ni–Cu ores. Econ. Geol., v.87, pp.975–1004.

Pinto, V.M., Hartmann, L.A., and Wildner, W. (2011) Epigenetic hydrothermal origin of native copper and supergene enrichment in the Vista Alegre district, Paraná basaltic province, southernmost Brazil. Int. Geol. Rev., v.53, pp.1163-1179.

Plank, T. and Langmuir, C.H. (1998) The chemical composition of subducting sediment and its consequences for the crust and mantle. Chem. Geol., v.145, pp.325–394.

Rad'ko, V.A. (1991) Model of dynamic differentiation of intrusive Traps at the Northwestern Siberian Trap. Geol. Geofiz., v.32, pp.19–27.

Radhakrishna, B.P. and Pandit S.A. (1973) On the occurrences of native copper in Deccan Traps. Dept. Mines Geol., Gov. Karnataka Rep., v.73, pp.283–286.

Raja Rao, C.S., Sahasrabudhe, Y.S., Deshmukh, S.S. and Raman, R. (1978) Distribution, structure and petrography of the Deccan Trap, India. Report Geological Survey of India, 43pp.

Rajamani, V. and Naldrett, A.J. (1978) Partitioning of Fe, Co, Ni and Cu between sulfide liquid and basaltic melts and the composition of Ni-Cu sulfide deposits. Econ. Geol., v.73, pp.82–93.

Ray, R.., Shukla, A.D., Sheth, H.C., Ray, J.S., Duraiswami, R.A., Vanderkluysen, L. and Mallik, J. (2008) Highly heterogeneous Precambrian basement under the central Deccan Traps, India: direct evidence from xenoliths in dykes. Gond. Res., v.13, pp.375–385.

Rehkämper, M., Halliday, A.N., Fitton, J.G., Lee, D.-C., Wieneke, M. and Arndt, N. T. (1999) Ir, Ru, Pt, and Pd in basalts and komatiites: new constraints for the geochemical behavior of the platinum-group elements in the mantle. Geochim. Cosmochim. Acta, v.63, pp.3915–3934.

Ripley, E.M., Brophy, J.G. and Li, C. (2002) Copper solubility in a basaltic melt and sulfide liquid/silicate melt partition coefficients of Cu and Fe. Geochim. Cosmochim. Acta, v.66, pp.2791–2800.

Roy, B.C. (1953) A Note on the occurrence of native copper in Deccan traps near Bhayavadar, Madhya Saurashtra. Geol. Surv. India, GSI-CHQ-12961, pp.1–8.

Rudnick, R.L. and Gao, S. (2003) Composition of the continental crust. *In:* H.D. Holland, and K.K. Turekian (Eds.), The Crust. Treatise on Geochemistry, Elsevier, Amsterdam, v.3, pp.1–64.

Segev, A. (2002) Flood basalts, continental break-up and the dispersal of Gondwana: evidence for periodic migration of upwelling mantle flows (plumes). EGU Stephen Mueller Spec. Publ. Series, v.2, pp.171–191.

Sen, G. (1986) Mineralogy and petrogenesis of the Deccan Trap lava flows around Mahabaleshwar, India. Jour. Petrol. v.27, pp.627–663

Sen, G. (2001) Generation of Deccan trap magmas. Proc. Indian Acad. Sci. Earth and Planet. Sci., v.110, pp.409–432.

Seward, T.M. (1971) The distribution of transition elements in the system $CaMgSi_2O_6$-$Na_2Si_2O_5$-H_2O at 1000 bars pressure. Chem. Geol., v.7, pp.73–95.

Sheth, H.C. (2005) From Deccan to Réunion: no trace of a mantle plume. Geol. Soc. Amer. Spec. Papers, v.388, pp.477–501.

Sillitoe, R.H. (1997) Characteristics and controls of the largest porphyry copper-gold and epithermal gold deposits in the circum-Pacific region. Australian Jour. Earth Sci., v.44, pp.373–388.

Song, X.Y., Zhou, M.F., Cao, Z.M., Sun, M. and Wang, Y.L. (2003) Ni–Cu–(PGE) magmatic sulfide deposits in the Yangliuping area, Permian Emeishan igneous province, SW China. Mineral. Deposita, v.38, pp.831–843.

Stanton, R.L. (1994) Ore elements in arc lavas. Oxford Monographs Geology and Geophysics, v.29, 391pp.

Sun, S.-S. and McDonough, W.F. (1989) Chemical and isotopic systematics of oceanic basalts: implications for mantle composition and processes. *In:* A.D. Saunders, and M.J. Norry (Eds.), Magmatism in the Ocean Basins. Geol. Soc. London, Spec. Publ., v.42, pp.313–345.

Venkatesan, T. R., Pande, K. and Gopalan, K. (1993) Did Deccan volcanism pre-date the Cretaceous/Tertiary transition? Earth Planet. Sci. Lett., v.119, pp.181–189.

Vijaya Kumar, K., Chavan, C., Sawant, S., Nagaraju, K., Kanakdande, P., Patode, S., Deshpande, K., Krishnamacharyulu, S.K.G., Vaideswaran, T. and Balaram, V. (2010) Geochemical investigation of a semi-continuous extrusive basaltic section from the Deccan Volcanic Province, India: implications for the mantle and magma chamber processes. Contrib. Mineral. Petrol. v.159, pp.839–852.

Vijaya Kumar, K., Laxman, M. B. and Nagaraju, K. (2018). Mantle source heterogeneity in continental mafic Large Igneous Provinces: insights from the Panjal, Rajmahal and Deccan basalts, India. *In:*S. Sensarma and B.C. Storey (Eds.), Large Igneous Provinces from Gondwana and Adjacent Regions, Geol. Soc. London, Spl. Publ., v.463, pp.87-116.

Wadia, D.N. (1975) Geology of India. Tata McGraw-Hill, New Delhi, 508pp.

Wang, C.Y. and Zhou, M.F. (2006) Genesis of the Permian Baimazhai magmatic Ni–Cu–(PGE) sulfide deposit, Yunnan, SW China. Mineral. Deposita, v.41, pp.771–783.

Wendlandt, R.F. (1982) Sulfide saturation of basalt and andesite melts at high pressures and temperatures. Amer. Mineral., v.67, pp.877–885.

Wilson, A. and Chunnett, G. (2006) Trace element and platinum group element distributions and the genesis of the Merensky Reef, Western Bushveld Complex, South Africa. Jour. Petrol., v.47, pp.2369–2403.

Wooden, J.L., Czamanske, G.K., Fedorenko, V.A., Arndt, N.T., Chauvel, C., Bouse, R.M. and Siems, D.F. (1993) Isotopic and trace-element constraints on mantle and crustal contributions to Siberian continental flood basalts, Noril'sk area, Siberia. Geochim. Cosmochim. Acta, v.57, pp.3677–3704.

Yuan, F., Zhou, T., Zhang, D., Jowitt, S.M., Keays, R.R., Liu, S. and Fan, Y. (2012) Siderophile and chalcophile metal variations in basalts: implications for the sulfide saturation history and Ni–Cu–PGE mineralization potential of the Tarim continental flood basalt province, Xinjiang Province, China. Ore Geol. Rev., v.45, pp.5–15.

Zhang, M., O'Reilly, S.Y., Wang, K.L., Hronsky, J. and Griffin, W.L. (2008) Flood basalts and metallogeny: the lithospheric mantle connection. Earth Sci. Rev., v.86, pp.145–174.

Zhang, Z., Mao, J., Chai, F., Yan, S., Chen, B. and Pirajno, F. (2009) Geochemistry of the Permian Kalatongke mafic intrusions, northern Xinjiang, northwest China: implications for the genesis of magmatic Ni-Cu sulfide deposits. Econ. Geol., v.104, pp.185–203.

(Received: 22 August 2017; Revised form accepted: 11 May 2018)