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Spinel chemistry from Madawara Mafic-Ultramafic Complex, Lalitpur District, Uttar Pradesh, India

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ABSTRACT

Spinel in peridotite of the Pipariya area in Madawara Mafic and Ultramafic Complex (MMUMC) occur as euhedral to subhedral inclusion within the silicates. They exhibit regular to irregular shape and is altered to ferritchromite to magnetite along the cracks and boundaries. Cr-spinel is characterised by high values of Cr# (79.7-98.4) and low Mg# and Al# values (i.e., 20.41-9.66 and 0.49-17.71, respectively) and are identified as Fe-chromite. Chemical discontinuity/zones between the core and rim can be observed in the analysed grain. The textural and chemical features of investigated suggest low- to sub greenschist facies metamorphism consistent with the estimated metamorphic equilibrium temperature of 500^0C-550^0C.

Mineral chemistry of these spinel suggests that spinel in peridotite of Pipariya in the Madawara Mafic and Ultramafic Complex depicts that these Cr-spinel may have been derived from boninitic related magmas at arc to suprasubduction zone tectonic setting at low degree of partial melting.

Keywords: Spinel, MMUMC, Madawara, Mineral chemistry, Peridotites

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INTRODUCTION

The study area is located approximately 10 km east of Madawara in the Lalitpur District of Uttar Pradesh, India and generally is known as the Madawara Mafic and Ultramafic Complex (MMUMC). Chemical and mineralogical studies on the MMUMC in the study area are rare. In this paper we examine the chemical variation and characteristics of the chromium-spinel from peridotites of the MMUMC from the study area.

Cr-spinel is an important petrogenetic indicator in ultramafic to mafic rocks. It is also extensively sensitive to bulk rock composition mineralogy and petrogenesis of host rocks (e.g., Irvin, 1965, 1976; Thayer, 1970; Evans and Frost, 1975; Dick, 1977; Frisk and Bence, 1980; Zao et al., 1997; Proenza et al., 1999; Apple et al., 2002; Devraju, et al., 2007; Rodder and Campbell, 1985). In addition to this, chemistry of Cr-spinel plays an important role in classifying mantle derived peridotites in terms of origin and tectonic setting (Dick and Bullen, 1984; Pal et al., 2008), record the equilibrium temperature and rate of crystallization in olivine-bearing rocks (Irvin, 1965; Jackson, 1969; Evans and Frost, 1975; Ozawa, 1985; Huge et al., 2002) and it also acts as stress indicator and oxygen barometer in peridotites and other rocks (Mattioli and Woods, 1986; Woods and Virgo, 1989). Due to these characteristics, Cr-spinel can be used effectively as petrogenetic indicator and has potential to indicate the chemical character of the parent magma and / or mantle source.

REGIONAL GEOLOGY

The Bundelkhand Granite Massif (BGM) in Central India (Fig. 1), forms the part of the Precambrian Central Indian Shield and has been, known to contain relicts of older crust. The BGM represents the Archaean-Paleoproterozoic sequence of plutonic masses with sporadic supracrustal enclaves and metabasic rocks (Prakash et al., 1975; Mondal and Zainuddin, 1996).

The Archaean crust is represented by EW trending belts consisting of peridotite, pyroxenite, gabbro, amphibolite and metasedimentary rocks, which are intruded by Tonalite-Trondhjemite-Granodiorite (TTG) gneisses (Basu, 1986). The plutonic Bundelkhand massif includes several phases of deformed / undeformed coarse grain/porphyric granite, at least five phases of intrusions have been reported (Rehman and Zainuddine, 1993), such as amphibole-bearing granodiorite (Phase-I), porphyritic variety of biotite granite, coarse porphyritic granite and two phases of leucogranite represent the subsequent phases of intrusion. Recent geochronological data suggest that these undeformed multiphase granitoids were emplaced within a short span of time from 2.5 to 2.4 Ga (Mondal et al., 2002).

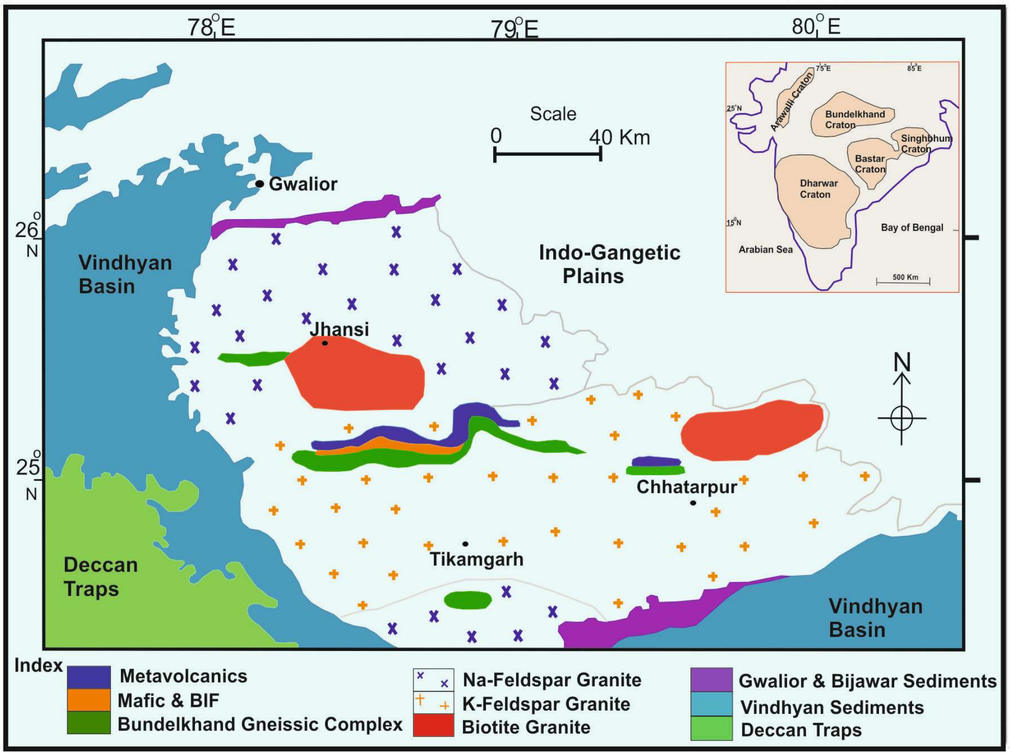

Fig. 1: Regional geological map of Bundelkhand Craton

The emplacement of Bundelkhand granite is followed by the extensive fracturing of the massif, especially in ENE-WSW and NE-SW directions accompanied by shearing and sinistral displacement of earlier elements (Basu, 1986). This shearing led to generation of extensive mono mineralic reef of quartz, fine grain granite and felsite along these pre-existing tensional fractures (Basu, 1986). At the end of intrusive acidic phase, the BGM experienced emplacement of basic dyke on a wide scale along NW-SE, NNW-SSE direction. The mafic dykes are mostly dolerites. Intensity of deformation and metamorphism grade is not as high as in nearby part of the shield area such as Aravalli and Sakoli-Sausor Belt (Basu, 1986; 2001).

LOCAL GEOLOGY

The mafic and ultramafic rocks of Piparyia form the eastern extension of the Madaura Ultrabasic Complex located at the southern hinge zone of Bundelkhand granite/gneiss complex overlain by early Proterozoic Bijawar sedimentary sequence in the south.

The rocks of investigated area belong to the Madaura Formation, but some rock types are missing in the area. The gneiss and metamorphosed ultramafic rocks form a concordant sequence. The ultramafic rocks comprising spinel peridotites are highly altered into serpentinized tremolite schist. Most of them were probably peridotite giving almost complete presence of minerals of serpentine and amphibole containing rare ilmenite, magnetite and abundant spinel, which are in contact with granitic gneiss.

Methodology and analytical techniques

After, a detailed literature survey of the geology and tectonic features of the area, the area under investigation was systematically mapped delineating the lithological unit present in the area and a geological map of the area was prepared (Fig. 2). The representative samples were collected and labelled from the outcrops for laboratory investigation. Thin and polished sections of the samples were prepared to examine their surface texture and mineralogy. All these samples were examined using

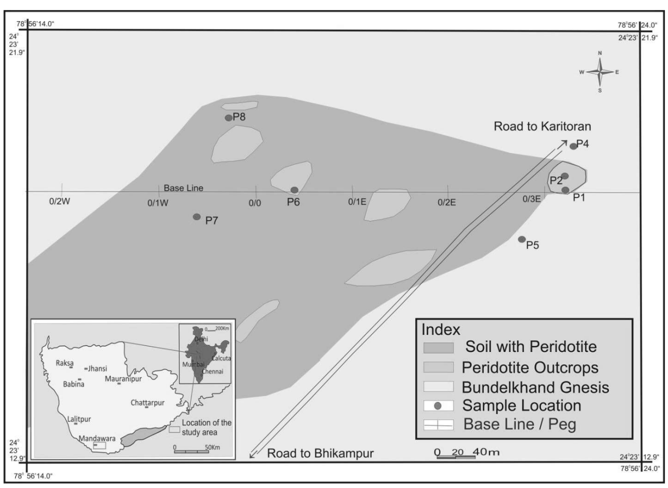

Fig. 2: Geological map of study area (Pipariya) in Lalitpur district, Uttar Pradesh, India

Cameca SX 100 electron microprobe having the wavelength-dispersive spectrometry (WDS) at Institute of Geology v.v.i., Academy of Sciences of the Czech Republic, Prague. Analytical conditions were as follows: 15 kV accelerating voltage, 20nA beam current and 2 µm beam diameter. A counting time of 10s was used for all elements. Synthetic and naturals minerals were used as standards. The Fe was determined as total iron (Carmichael and Nicholls, 1967) procedure based on stoichiometry was adopted for calculation of FeO and Fe_2O_3. The representative data together with Cr# [100/Cr (Cr+Al)], Mg# [100Mg / (Fe^{2+}+ Mg)] and Fe^{3+}# [100 Fe^{3+} / Cr+Al+Fe^{3+}] of chrome spinel is shown in Table 1.

Spinel chemistry

The back-scattered (BSE) image from peridotite characterise the alteration products of Cr-spinel (Fig. 3). The image displays strong zoning, dark area represents Cr/Al rich and Fe-poor composition of the core relative to the rims enriched in Fe and Mn. The microprobe analysis is given in Table 1. The spinel is characterized by high Cr_2O_3 (41.05– 51.55 wt. %) and low Al_2O_3 (0.20–7.92 wt. %), FeO (51.34–40.70 wt. %) and MgO (1.80–6.48 wt. %). Cr# varies from 0.79–0.98.

Chromite composition is presented on Cr/ (Cr+Al) vs. Fe/(Fe+Mg) diagram (Fig. 4). The core and rim compositions of chromite define a trend of increasing Fe with near constant Cr/Al ratio. There is also a small but systematic increase in Ti with Fe. Overall spinel composition shows enrichment in Fe and depletion in Al and Mg.

The analysed spinels are also plotted at triangular plot of Cr-Al-Fe^{3+} showing that the analysed grains fall in Fe-chromite field and analysis of the chromite is plotted in overlapping compositional field of boninite, ophilitic and komatiitic (Stevens, 1944; Barnes and Roeder, 2001) (Fig. 5).

The Cr# vs. TiO_2 plot shows that chromite falls very close to boninite field (Dick and Bullen, 1984; Arai, 1992; Jan and Windley, 1990) (Fig. 6). In Al_2O_3 versus TiO_2 plot chromite indicates a genetic link with either near Arc low Ti to suprasubduction peridotite field Kamenetsky et al. (2001) (Fig. 7). The bivariant plot of Al_2O_3 versus Fe^{2+} / Fe^{3+} also indicates that chromite falls in overlapping field of suprasubduction peridotite and volcanic spinel Kamenetsky et al. (2001) (Fig. 8).

Table 1: Electron Microprobe analysis of spinel

Sample	P/7	P/7	P/7	P/7	P/7	P/7	P/7	P/7	P/7	P/7	P/7
Mineral	spinel	spinel	spinel	spinel	spinel	spinel	spinel	spinel	spinel	spinel	spinel
Data set/ Point	26 / 1	27 / 1	28 / 1	29/1core	30/1rim	31 / 1	32 / 1	33 / 1	34 / 1	35 / 1	38 / 1
SiO_2	0.00	0.00	0.01	0.01	0.01	0.00	0.02	0.00	0.04	0.00	0.00
TiO_2	0.41	0.81	0.72	0.51	0.86	0.83	0.84	0.93	0.83	0.95	0.66
Al_2O_3	7.92	0.81	0.57	7.79	1.57	1.31	0.46	0.20	1.20	2.04	1.29
Cr_2O_3	46.38	45.00	44.94	51.55	43.49	44.67	44.01	43.28	44.00	44.97	41.05
FeO	40.70	48.56	48.83	36.21	49.42	48.87	50.88	51.34	48.11	46.83	48.99
MnO	0.26	0.53	0.63	0.00	0.39	0.47	0.45	0.52	0.31	0.27	2.05
MgO	1.40	0.55	0.48	1.88	0.66	0.55	0.49	0.50	0.63	0.80	1.01
CaO	0.01	0.03	0.09	0.00	0.03	0.02	0.00	0.02	0.00	0.00	0.00
Total	97.12	96.35	96.38	97.98	96.48	96.84	97.20	96.87	95.19	95.90	95.08
O	4	4	4	4	4	4	4	4	4	4	4
Si	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Ti	0.01	0.02	0.02	0.01	0.03	0.03	0.03	0.03	0.03	0.03	0.02
Al	0.35	0.04	0.03	0.34	0.08	0.06	0.02	0.01	0.06	0.10	0.06
Cr	1.38	1.45	1.45	1.50	1.40	1.43	1.42	1.41	1.43	1.44	1.35
Fe	1.28	1.66	1.67	1.11	1.68	1.66	1.74	1.77	1.66	1.58	1.70
Mn	0.01	0.02	0.02	0.00	0.01	0.02	0.02	0.02	0.01	0.01	0.07
Mg	0.08	0.03	0.03	0.10	0.04	0.03	0.03	0.03	0.04	0.05	0.06
Ca	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Na	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
K	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Fe^{3+}	0.25	0.48	0.50	0.15	0.50	0.48	0.53	0.55	0.48	0.44	0.57
Fe^{2+}	1.03	1.18	1.18	0.96	1.18	1.18	1.21	1.21	1.18	1.15	1.14
Total	3.12	3.23	3.24	3.07	3.24	3.23	3.25	3.26	3.23	3.21	3.27
Cr #	79.71	97.39	98.14	81.61	94.89	95.81	98.47	99.32	96.09	93.66	95.52
Mg #	7.09	2.77	2.43	9.66	3.27	2.75	2.41	2.47	3.18	4.04	5.22
Fe #	8.37	15.33	15.70	5.08	15.83	15.27	16.69	17.40	15.29	14.03	18.18
Al #	17.71	1.97	1.39	17.00	3.81	3.17	1.12	0.49	2.95	4.93	3.19
Fe^{3+}/Fe^{2+}	0.24	0.41	0.42	0.16	0.42	0.41	0.44	0.46	0.41	0.38	0.50
Fe^{2+} / Fe3+	4.08	2.43	2.38	6.44	2.37	2.44	2.27	2.19	2.44	2.62	2.01

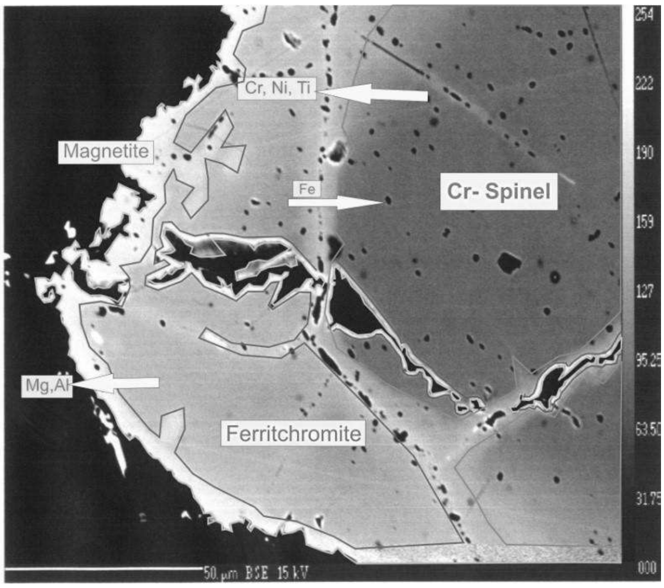

Fig. 3: BSE image showing chemical changes in Cr-Spinel during alteration and metamorphism

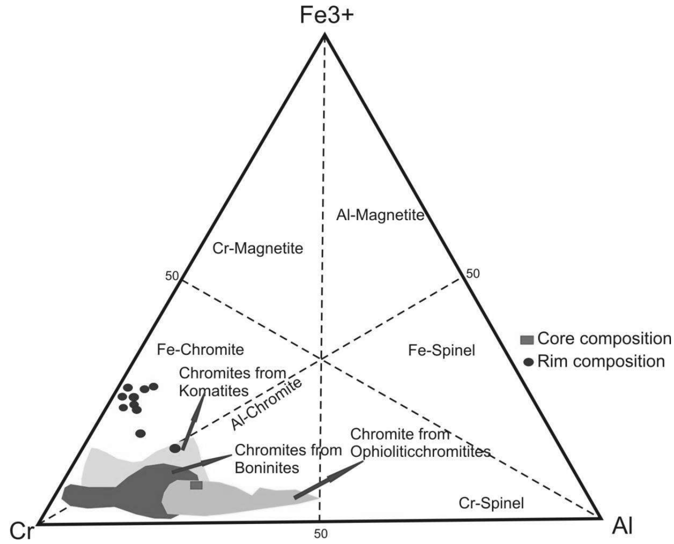

Fig. 5: Trivalent cation plot of chromite of Piparyia area in comparison with boninitite, ophiolite and komatitic (after Stevens, 1944; Barnes and Roeder, 2001)

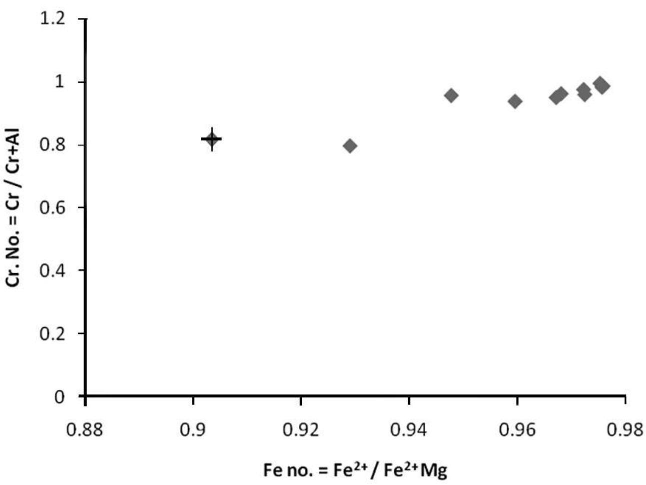

Fig. 4: Fe# vs. Ce# plot of chromite composition from Pipariya area, showing variation of Cr# within a small range, whereas Fe# showing wide variation

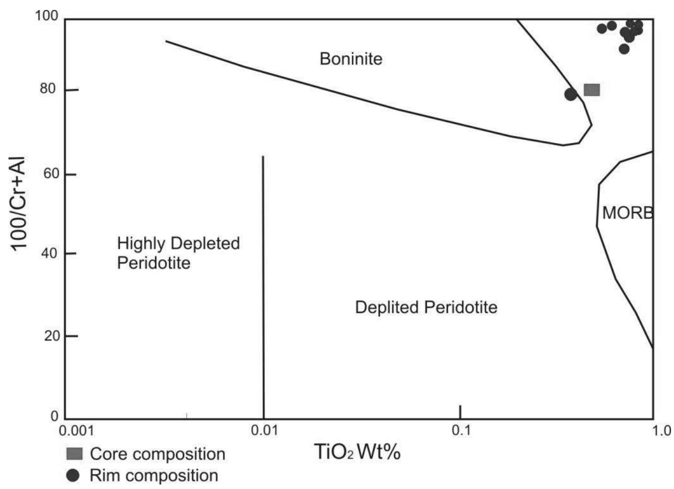

Fig. 6: Compositional plot of TiO_2 vs. Cr# showing near boninitic field for chromite after Dick and Bullen (1984), Arai (1992), Jan and Windley (1990)

Texturally, Cr-spinel shows distinct zoning reflecting the chemical changes during different process. Metamorphic P-T condition and their relationship with spinel compositional changes are shown in (Fig. 9) (Evans and Frost, 1975; Suita and Streider, 1996; Sack and Ghiorso, 1991).

DISCUSSION

Alteration of spinel

The BSE image reflects the textural and compositional modification during the alteration process, which may be serpentinization due to regional metamorphism or by any other processes as well. In an ideal case, optically zoned Cr-spinels consist of a dark grey chromite core, followed by an irregular ferritchromite zone showing light grey colour and a grey-white magnetite rim. Due to gradual transformation of chromite to ferrite-chromite, magnetite is the final product of this alteration. However, Cr-spinel investigated in the present study clearly shows unaltered dark chromite core followed by light-grey ferrite-chromite, which is evenly rimmed by magnetite (Fig. 3).

The analysed Cr- spinel from the investigated area confirms the enrichment of Cr and Al at the core and Fe at the rim. The core of Cr-spinel is high in Cr_2O_3 (51.55 wt. %) and

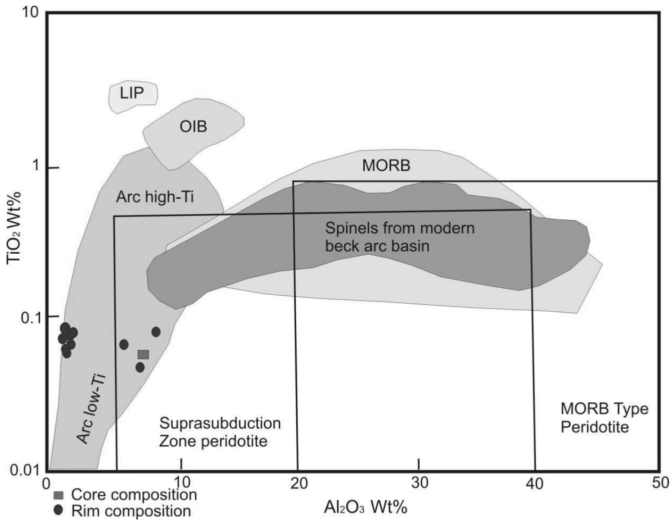

Fig. 7: Tectonic discrimination diagram showing TiO_2 vs. Al_2O_3 variation with respect to modern day tectonic setting (Kamenetsky et al., 2001)

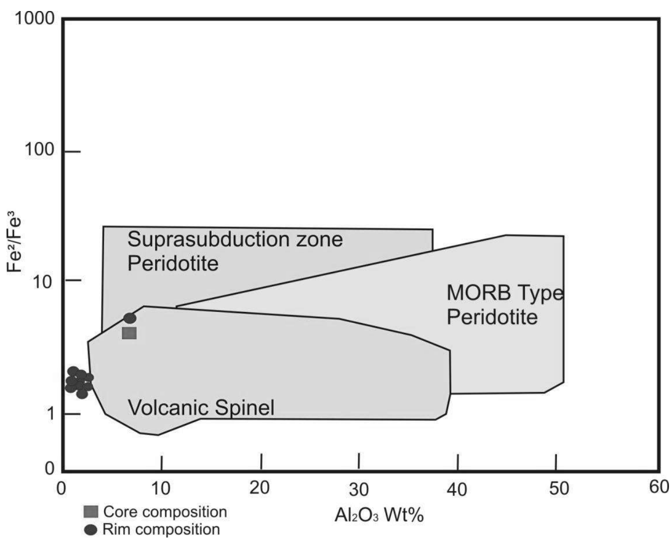

Fig. 8: Tectonic discrimination diagram showing Fe^{2+}-Fe^{3+}-Al_2O_3 variations with respect to modern day tectonic settings (after Kamenetsky et al., 2001)

Al_2O_3 (7.79 wt. %) while rim of Cr-spinel shows low Cr_2O_3 (i.e. from 51.55 wt. % to 43.49 wt. %) and Al_2O_3 (i. e., from 7.79 wt. % to 1.57 wt. %) with enrichment of FeO from 36.21 wt. % to 49.42 wt. %.

The extant of exchange and replacement reactions seems to be a function of metamorphic fluid access and fluid-rock ratio; where fluid rock interactions are fluid dominant, spinel is almost destroyed, and undergoes extensive Al loss to the surrounding silicate minerals (Barnes, 2000). The common preservation of magmatic Cr-spinel implies small fluid rock ratio in the investigated Cr-spinel from the study area.

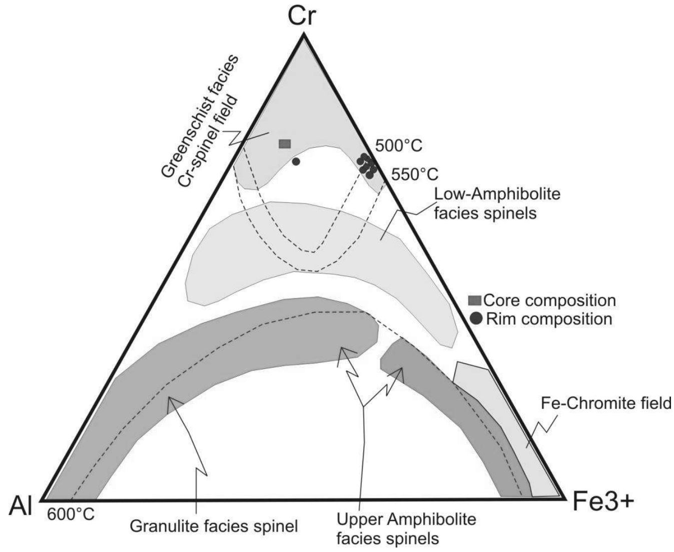

Fig. 9: Compositional change in chrome spinel of Pipariya area in terms of Cr-Fe^{3+}-Al plot. Metamorphic facies are after Evans and Frost (1975), Suita and Streider (1996). Spinel stability field for chromite / equilibrium with olivine of composition are after Sack and Ghiorso (1991).

Preservation of unaltered Cr-spinel cores in the peridotite of Pipariya in the Madawara Mafic and Ultramafic Complex indicate that full equilibrium has not been attained, possibly due to small fluid rock ratio.

The Cr-spinel equilibrated below 500–550^{o}C, retains original Cr-content, but Mg# values are substantially lowered by Fe-Mg exchange with silicates. The investigated ferrite-chromite zones preserve high Cr content (41.05–46.38 wt. %) close to those of magmatic core but apparently low Fe#, accordingly marking the range of metamorphism 550–600^{o}C where igneous composition is considerably modified by equilibration between chromite core, ferrite-chromite and surrounding silicates in the present study area.

Grade of metamorphism

Textural variation of spinel during metamorphism can be related to the grade of metamorphism (Barnes, 2000), the textural and chemical changes of primary spinel can be depicted from Fig. 3. In rocks of sub greenschist to lower greenschist facies, outer thin magnetite rims develop, which are often incomplete and have sharp contact with chromite core. With more extensive fluid interaction i.e., in mid-greenschist facies, magnetite alteration zones develop around the margins and along the fractures of Cr-spinel. In mid amphibolite facies rocks, Cr-spinel grains are almost completely replaced by magnetite and ferrite-chromite cores are rare. On the bases of these observations, textural and chemical characteristic of the studied Cr-spinel in peridotite of Pipariya in the Madawara Mafic and Ultramafic Complex matches those of the low to upper greenschist facies metamorphism consistent with the estimated metamorphic equilibrium temperature of 500–550°C (Evans and Frost, 1975; Suita and Streider, 1996) (Fig. 9).

Petrogenesis and geotectonics evolution

Spinel Cr# or Al_2O_3 values are commonly used to constrain the nature of mantle peridotite source and the degree of partial melting (Jaques and Green, 1980). Spinel with high Cr# are crystallised from highly magnesian magmas (boninitic type) at high degree of partial melting. The analysed spinel has Cr# 79–98.4, which is comparable with those of boninitic affinity, i.e. Cr# 80–90 (Rodder and Reynolds, 1991), further Figs. 5 and 6 also reflect the boninitic affinity of the studied spinel. The high Cr# (=80) of Cr-spinel of mantle origin is interpreted as a genetic relationship with boninitic and related magmas.

The high TiO_2 of the studied spinel (0.41–0.95 wt. %) can be comparable with those from stratiform complex, Alaskan type complex and mafic-ultramafic rocks from deeper level of island arc which generally contain = 3 wt. % TiO_2 (Jan and Windley, 1990). Further, the TiO_2 vs. Cr# and Al_2O_3 vs. Fe^{2+} / Fe^{3+} relationship (Figs.7 and 8) clearly show that studied spinel plots close to the field of arc related and suprasubduction zone peridotite.

CONCLUSION

Spinel in the peridotite of Pipariya in the Madawara Mafic and Ultramafic Complex are variably altered, providing opportunity to evaluate the petrogenesis and tectonic setting. They are typically zoned with unaltered core to Cr-magnetite rims through ferrite-chromite transitional zones. Compared to cores, the rims are depleted in Al, Mg, and Cr while enriched in Fe^{3+}. Metamorphism is the major control on the chemical modification of the investigated spinel and serpentinization to some extent. The textural and chemical features of investigated suggest low to upper greenschist facies metamorphism consistent with the estimated metamorphic equilibrium temperature of 500–550°C.

TiO_2 vs. Cr# and Al_2O_3 vs. Fe^{2+} / Fe^{3+} variation diagram of Cr-spinel in peridotite of Pipariya in the Madawara Mafic and Ultramafic Complex in comparison to modern day tectonic setting depicts that these Cr-spinel may have been derived from boninitic related magmas at arc to suprasubduction zone tectonic setting at low degree of partial melting.

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