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Mineral compositional studies of slag from Galla village, Uttarakhand, India

Mineral and chemical compositional studies of ancient iron and its slag for their characterization from various parts of India have been carried out by different workers^{1,2}. One of the recent studies from India was on iron slag from Kakching, Manipur³. Mineralogical and elemental studies on slags throw light on the prevailing conditions and methods used to extract metals out of enriched rocks by ancient workers. Abundance of iron slags in Kumaon region, Uttarakhand, India might suggest that a close interaction did exist between the Ganga valley and Kumaon in ancient times, and probably metal was one of the main commodities supplied to the Ganga valley for urbanization⁴. Here, we discuss the findings of the compositional studies carried out on the slag samples of Galla village, Nainital district, Uttarakhand and the implications on metallurgical methods adopted by ancient workers of Kumaon Himalaya.

Slags are found strewn along the slope of the terrace of Galla village (Survey of India Toposheet No. 53 O/11). The geological setting of the area comprises Proterozoic Lesser Himalayan sequence with metamorphosed siliceous limestone and phyllites of Betalghat Formation (Jaunsar Group) underlain by Palaeoproterozoic quartzites of Ramgarh Group⁵. Iron mineralization in the rocks of the area occurs as occasional and minor magnetite-rich layers in phyllites and siliceous lime-

stone of Betalghat Formation. Few old workings were noticed in the vicinity of the rock exposures in the higher reaches of the terrace of Galla village, which indicate mining activities by local villagers in the past. Perhaps they used to extract iron metal from these rocks. Mineralogical studies were performed through optical microscopy and electron probe micro analysis (EPMA), whereas chemical analyses of the slag were carried out using X-ray fluorescence (XRF) and atomic absorption spectra (AAS) methods for major oxides and trace elements respectively. EPMA of the slag was carried out in the EPMA Laboratory of Geo-

logical Survey of India (GSI), Faridabad using CAMECA SX 100 Electron Microprobe. The thin section to be probed was coated with carbon to conduct away charges on the surface caused by electron bombardment during analysis. The analyses of silicate and oxide phases were done at 15 and 20 kV respectively. Prior to analysis, the calibration was done using natural mineral and pure metal standards. The diameter of the electron beam was kept at 1 μ m.

Physically, these slags are brownish to black in colour (Figure 1) with numerous angular to sub-rounded pits. Microscopically, the slag consists dominantly of



Figure 1. Slags collected from Galla village, Uttarakhand, India.

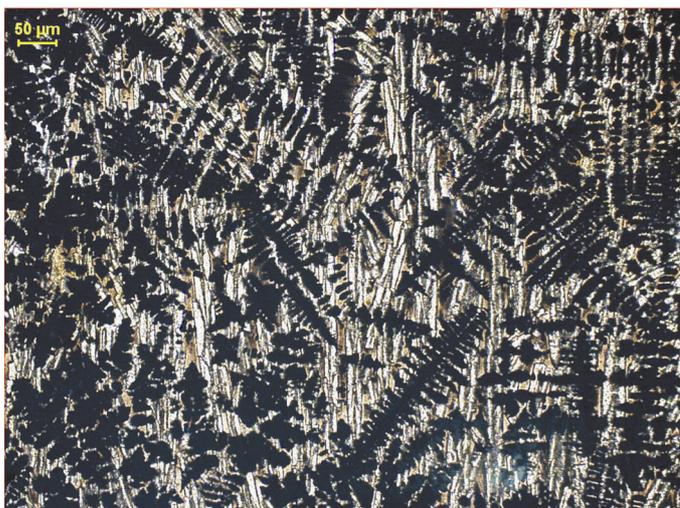


Figure 2. Opaques with 'feather' pattern along with fayalite in plane-polarized transmitted light (5× magnification).

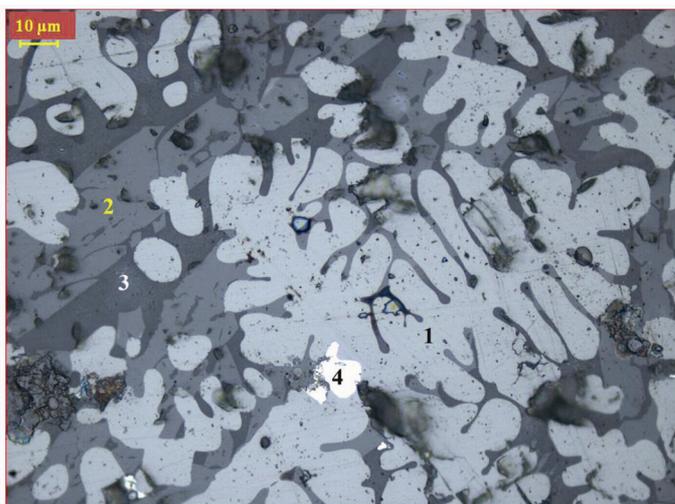


Figure 3. Magnetite (1), fayalite (2), glassy phase (3) and metallic iron (4) in reflected light ore microscopy (50× magnification).

black opaques present in feathered pattern and fayalite occupies the interstices in the opaques (Figure 2). Fayalite occurs as thin bladed flakes around the opaques. Under higher magnification, a glassy phase is also seen along with fayalite. The opaques, under reflected light microscopy, are grey with brownish tinges, isotropic under crossed polars, low reflectivity with well to moderate polished surfaces and are identified as magnetite. Few grains of metallic iron show bright white colour and higher reflectivity than the surrounding magnetite grains (Figure 3). Figure 4 shows the BSE image of various phases of slag.

Table 1 presents the chemical analyses of the slag (major oxides and trace elements). The XRF and AAS analyses show high amounts of Al, Mg, K, Mn, Ca and moderate P and S content in the slag. Table 2 presents representative analyses of magnetite, fayalite, metallic iron and silicate glass phases from the slag sample. The magnetite grains are consistently seen to contain on an average 31.16% FeO_(c) and 69.24% Fe₂O_{3(c)}, whereas the glassy phase consists of ~35.8–37.5% SiO₂ with concentrations of 18–21% Al₂O₃, 7.9–10.2% CaO, 18–23% FeO, about 2% MnO and 1.7–1.92% P₂O₅ with restricted concentrations of K₂O (about 7.5%). Fayalite contains about 57–59% FeO with about 5% MnO and 29–30% SiO₂. On the other hand, native iron blebs show average Fe_(m) to be 94.59%. Minute inclusions in magnetite may have triggered fluorescence and contributed to higher calculated total in magnetite analyses, whereas presence of iron in sulphide phase may have yielded lower values of Fe in metallic iron as sulphur was not part of analysis protocol.

The mineral phase fayalite can absorb elements like Mn and Mg during high-temperature melting of the silicate gangue, which explains the higher proportions of MnO and MgO in this mineral phase. Studies on slags from ancient smelting furnaces indicate that if the major gangue material is silica, the latter becomes the source for the formation of fayalite³. Kapilashrami *et al.*⁶ studied the formation of fayalite (Fe₂SiO₄) in slags through experiments in the Fe–O–Si system. Thermodynamic calculations have shown that two silicates (both orthosilicate and metasilicate) are likely to be formed in the Fe–O–Si system. However, with higher temperatures prevailing in

Table 1. Major oxides and trace element composition of Galla slag

Major oxides	Concentration (wt%)	Trace elements	Concentration (ppm)
SiO ₂	29.60	Cu	28
Al ₂ O ₃	4.66	Pb	<20
Fe ₂ O ₃	52.58	Zn	30
CaO	6.63	Ni	<10
MgO	1.4	Co	<10
Na ₂ O	0.08	Mn	19100
K ₂ O	1.73	Cd	<5
MnO	1.51	Ag	<5
TiO ₂	0.11	As	<100
P ₂ O ₅	0.91	Au	<0.05
BaO	0.057		
SrO	0.012		
Cr ₂ O ₃	0.009		
ZrO ₂	0.004		
LOI	0.11		
SO ₃	909 ppm		

Table 2. Electron probe micro analysis results of different phases in Galla slag

Variant	Fayalite							Glassy phase							Magnetite			Metallic iron																
	1	2	3	Average	1	2	3	1	2	3	4	Average	1	2	3	1	2	3	1	2	3	Average												
	SiO ₂	29.93	30.15	29.43	29.84	36.68	37.52	35.88	36.18	36.57	0.26	0.18	0.31	0.25	0.1	0.08	0.18	0.12	0.17	0.23	0.44	0.28	20.48	19.78	21.08	19.06	20.1	0.93	0.94	0.93	0.93	0	0	0
Al ₂ O ₃	58.68	59.48	57.81	58.66	20.43	18.13	19.35	22.97	20.22	93.15	93.56	93.68	93.46	121.02	123.66	120.19	121.62	58.68	59.48	57.81	58.66	20.43	18.13	19.35	22.97	20.22	93.15	93.56	93.68	93.46	121.02	123.66	120.19	121.62
(FeO)	-	-	-	-	-	-	-	-	-	31.05	31.19	31.23	31.16	-	-	-	-	-	-	-	-	31.05	31.19	31.23	31.16	-	-	-	-	-	-	-	-	
FeO _(e)	-	-	-	-	-	-	-	-	-	69.00	69.31	69.40	69.24	-	-	-	-	-	-	-	-	69.00	69.31	69.40	69.24	-	-	-	-	-	-	-	-	
Fe ₂ O _{3(c)}	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Fe _(metallic)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
CaO	1.15	1.15	0.87	1.06	10.26	9.9	9.45	8.95	9.64	0.03	0.05	0.08	0.05	0.18	0.07	0.09	0.11	1.15	1.15	0.87	1.06	10.26	9.9	9.45	8.95	9.64	0.03	0.05	0.08	0.05	0.18	0.07	0.09	0.11
MgO	3.97	4.18	4.9	4.35	0.35	0.19	0.17	0.26	0.24	0.31	0.21	0.3	0.27	0.08	0	0.03	0.04	3.97	4.18	4.9	4.35	0.35	0.19	0.17	0.26	0.24	0.31	0.21	0.3	0.27	0.08	0	0.03	0.04
Na ₂ O	0.02	0	0	0.01	0.9	0.94	0.96	0.87	0.92	0.02	0	0.01	0.01	0.01	0.02	0.03	0.02	0.02	0	0	0.01	0.9	0.94	0.96	0.87	0.92	0.02	0	0.01	0.01	0.02	0.03	0.02	
K ₂ O	0	0.02	0.02	0.01	7.38	8.1	7.73	7.44	7.66	0.01	0.04	0.05	0.03	0.01	0.01	0	0.01	0	0.02	0.02	0.01	7.38	8.1	7.73	7.44	7.66	0.01	0.04	0.05	0.03	0.01	0	0.01	
MnO	5.79	5.83	5.43	5.68	2	1.61	1.6	2.13	1.84	2.26	1.97	1.83	2.02	0	0	0.06	0.02	5.79	5.83	5.43	5.68	2	1.61	1.6	2.13	1.84	2.26	1.97	1.83	2.02	0	0	0.06	0.02
TiO ₂	0.07	0.07	0.03	0.06	0.17	0.12	0	0.04	0.08	0.13	0.37	0.39	0.30	0.06	0.03	0	0.03	0.07	0.07	0.03	0.06	0.17	0.12	0	0.04	0.08	0.13	0.37	0.39	0.30	0.06	0.03	0	0.03
P ₂ O ₅	0.09	0.18	0.25	0.17	1.92	1.79	1.85	1.78	1.84	0	0	0.01	0	0	0	0.02	0.01	0.09	0.18	0.25	0.17	1.92	1.79	1.85	1.78	1.84	0	0	0.01	0	0	0	0.02	0.01
BaO	0.24	0.09	0.05	0.13	0.04	0	0.3	0.11	0.11	0	0	0	0	0	0.05	0	0.02	0.24	0.09	0.05	0.13	0.04	0	0.3	0.11	0.11	0	0	0	0	0	0.05	0	0.02
ZnO	0.07	0.06	0.01	0.05	0	0	0	0.03	0.01	0	0	0	0	0	0.22	0	0.07	0.07	0.06	0.01	0.05	0	0	0	0.03	0.01	0	0	0	0	0.22	0	0.07	
Cr ₂ O ₃	0.03	0	0	0.01	0.02	0	0	0.006	0.01	0.02	0.01	0	0.01	0.29	0.06	0.24	0.20	0.03	0	0	0.01	0.02	0	0	0.006	0.01	0.02	0.01	0	0.29	0.06	0.24	0.20	
F	0	0.16	0	0.05	0.06	0.2	0	0	0.07	0.01	0	0	0	0.08	0	0.03	0.03	0	0.16	0	0.05	0.06	0.2	0	0	0.07	0.01	0	0	0.08	0	0.03	0.03	
Cl	0.01	0	0	0	0	0	0	0	0	0	0	0.02	0.01	0	0.01	0.01	0.01	0.01	0	0	0	0	0	0	0	0	0	0	0	0.01	0.01	0.01	0.01	
Total	100.22	101.6	99.24	100.30	100.69	98.28	98.39	99.83	99.31	104.03	104.27	104.56	104.29	121.83	124.21	120.85	122.31	100.22	101.6	99.24	100.30	100.69	98.28	98.39	99.83	99.31	104.03	104.27	104.56	104.29	121.83	124.21	120.85	122.31

(FeO): Determined by EPMA; (c): Calculated values of FeO and Fe₂O₃ in magnetite.

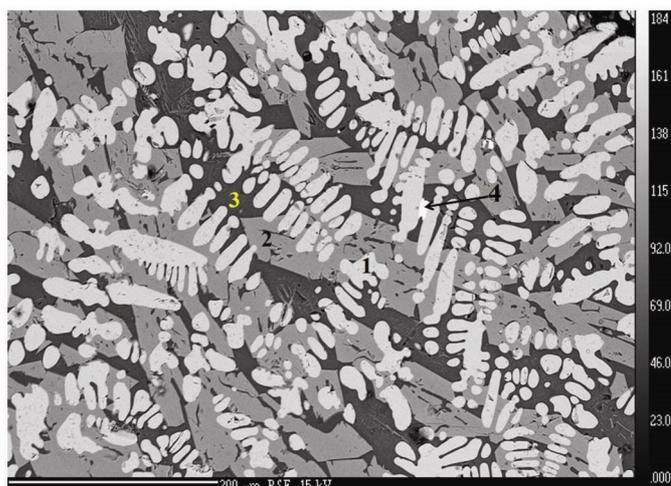


Figure 4. BSE image showing magnetite (1), fayalite (2), glassy phase (3) and metallic iron (4) phases in Galla slag.

the furnace, only fayalite (orthosilicate) in liquid form can be the stable phase. The temperature in the furnace may have reached about 1200°C, as the melting point of fayalite is around 1205°C with a FeO–Fe₂SiO₄ eutectic point of melting at 1177°C (ref. 3). The fayalite in the slag is formed synthetically from melting of silicate rock and rapid crystallization thereafter. The silicate melt thus formed is richer in Fe, and chills instantaneously forming a high-temperature mineral phase (fayalite) along with a quenched glassy matrix.

Studies on ancient slags worldwide^{7–10} have shown that the proportions of phosphorus are in the range 0.05–0.5 wt%, with levels up to 1.0 wt%. The phosphoric content in Galla slag is 0.91 wt%, which is on the higher side. The moder-

ately higher levels of P in Galla slag may be explained due to the presence of fayalite in good amount, which has a lesser dephosphorization efficiency than the common iron-bearing slags. However, moderate to high P may indicate that perhaps flux (limestone) was not used in the charge of ancient Indian bloomer furnaces for producing iron metal^{3,11}.

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Spatial distribution of suspended particulate matter in the Mandovi and Zuari estuaries: inferences on the estuarine turbidity maximum

An estuary is a region where a river meets the sea. In these estuarine regions there exists a strong physio-chemical and compositional gradient in the water properties, that varies rapidly from freshwater to sea water^{1,2}. Estuaries are important areas as they filter out suspended particulate matter (SPM), sediments and pollutants from the rivers before entering the sea and keep the

coastal seas healthy. The concentration of SPM varies from river end to sea end of the estuary, and high SPM concentrations along the transect are controlled by several factors, including the action of tides, gravity circulation, density stratification, resuspension and flocculation, or due to the combined action of one or more of these forces^{3–5}. Within the estuary there exists a distinctive zone with

high concentrations of SPM compared to the surrounding water in the seaward or landward side, called estuarine turbidity maximum (ETM)². These zones are useful as fish lay eggs and larvae thrive because of abundant food and are protected due to masking⁶. However, excess SPM in ETM with high organic content may give rise to bacterial action reducing dissolved oxygen from water, leading to