Ancient iron making process at Naikund, Vidarbha region of India: a thermochemical analysis of megalithic iron smelting

P. P. Deshpande*, V. S. Kathavate, N. K. Nath and V. S. Shinde

This study systematically demonstrates the ancient iron-making process in one of the earliest iron-smelting sites in India, and Naikund, Vidarbha region, dating as far back as 900 BC. During the process, the maximum temperature attained in the Naikund furnace was estimated to be ~1150–1250°C in the reaction zones where solid-state reduction of iron followed by separation of the low-melting slag phase and metallic iron were predominant. The low melting point of the slag phase is possibly due to the addition of sand or silica and limestone in the furnace during the iron-making process. Furthermore, mass balance studies performed using the Rist diagram superimposed with the Fe–C–O stability diagram revealed that the minimum charcoal rate was about 1900 kg/tonnes of iron produced. It can be anticipated that the porous, semi-solid metallic iron is hammered to produce various objects used for hunting and agriculture. The thermochemical analysis of one of the earliest iron-smelting sites in India provides evidence of the ancient iron-making processes in the country. This study further opens up multitudes of possibilities to analyse ancient metallurgical structures in India.

Keywords: Ancient iron-making process, mass balance studies, slag phase, thermal energy, thermochemical analysis.

IT is believed that the production and use of ferrous products in the Indian subcontinent dates back to the Palaeolithic Age (i.e. 2nd millennium BC). Archaeological excavations conducted at Naikund, one of the earliest iron-smelting megalithic sites, 42 km northeast of Nagpur, Maharashtra, India (lat. 21.36, long. 79.19) (see Annexure 1) have provided valuable evidence of an iron-smelting furnace complete with tuyere, indicating that the origin of ferrous metallurgy is a product of indigenous development and simultaneous beginning of the Iron Age at more than one centre in the Indian subcontinent[1–4]. This important discovery of the Naikund site led the archaeologists and metallurgists to estimate that this is the only ancient iron-smelting site in India, which is further reflected in all the essential features of the iron-smelting technology. Our previous observations on metallographic investigations of wrought iron samples from Mahurjhari, Naikund, Bhagimohari, and Khaiwada in the Vidarbha region of Maharashtra revealed that the iron objects obtained from these sites must have undergone identical thermomechanical treatments, further indicating the evidence for ancient steel-making and hardening treatment around 900 BC (refs 5–7). To the best of our knowledge, despite the above studies, the underlying mechanisms (or technology) of the steel-making process via the smelting of iron ore are not understood in detail. Due to slag phase formation during the iron-smelting process, it would be interesting to estimate the temperatures corresponding to the slag phase formation along with reactions corresponding to the temperatures and mass balance.

Keeping this in view, we performed a thermochemical analysis on the slag phase formation during the iron-smelting process in the Megalithic furnace at Naikund. Figure 1 shows a model of the Naikund furnace at Deccan College, Pune, Maharashtra, and its schematic drawing[4]. The supply of air was controlled through clay tubes known as tuyeres with the help of bellows.

Experimental analysis

Thermochemical analysis

The thermochemical process in iron-making consists of a counter current reaction in which raw material flows downward, while supply of hot gas in the upward direction (i.e. opposite to the flow of raw material). The process also involves partial melting and separation of impurities such as

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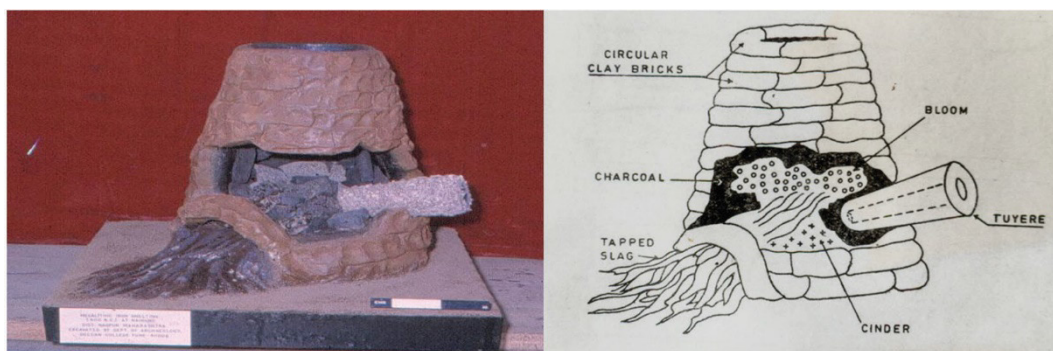*For correspondence. (e-mail: ppd.meta@coeptech.ac.in)

Figure 1. Model of the Naikund furnace at Deccan College, Pune, India, and its schematic drawing (from Gogte[4]).

Table 1. Important reactions considered for the iron-making process

Reaction no.	Reaction	$\Delta G° = \Delta H - T\Delta S$ (J/mol)
Reduction of iron oxide		
1.	$3Fe_2O_3 + CO = 2Fe_3O_4 + CO$	$-33096 - 54.04T$
2.	$Fe_3O_4 + CO = 3FeO + CO_2$	$29904 - 38.44T$
3.	$FeO + CO = Fe + CO_2$	$-17598 + 21.56T$
Charcoal combustion		
4.	$C + O_2 = CO_2$	$-395640 - 0.84T$
5.	$C + 0.5O_2 = CO$	$-111700 - 88T$
Calcination of limestone		
6.	$CaCO_3 = CaO + CO_2$	$169050 - 144.5T$
Boudouard or solution loss reaction		
7.	$C + CO_2 = 2CO$	$172240 - 174T$
Melting and solidification		
8.	[Solid slag] $\Leftrightarrow$ {liquid slag}	$255{,}000$ (approx.)

silica, limestone or calcium oxide, and trace amounts of other oxides. Table 1 shows the important reactions in the iron-making process.
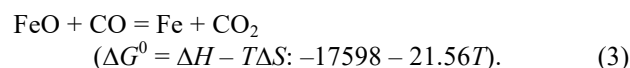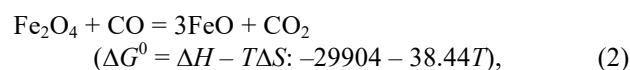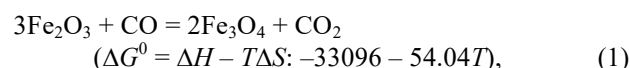
Combustion of charcoal

The combustion process of charcoal to form carbon monoxide (CO) and carbon dioxide (CO_2), as shown by reactions (1) and (2) in Table 1, takes place in the tuyere zone at the bottom of the furnace. The main reducing agent in the reaction is CO, which is formed by the partial oxidation of carbon, while the complete oxidation of CO_2 is expected to provide high thermal energy, possibly due to the high exothermic reaction.

Being a reducing gas, CO removes oxygen (O) from iron oxide (Fe_2O_3) present in the iron ore and thus sets free pure iron (Fe). However, CO_2 being inert during the process, does not react with Fe_2O_3. The complete conversion of carbon (C) into CO_2 is possible due to the excess supply of oxygen. Therefore, to partially oxidise charcoal to CO, it is essential to maintain a sub-stoichiometric and optimum supply of oxygen and charcoal in the furnace. However, the caveat here is that charcoal or C combustion provides both reducing gas and heat energy for the process, and the

heat produced by CO_2 formation is much higher than that produced by CO formation (see the enthalpy difference in the reactions mentioned below). Therefore, the formation of CO_2 is essential to attaining the required temperature for the melting or partial melting of the slag phase, though estimation of the quantity of CO_2 required (a stoichiometric proportion) is a timely topic and beyond the scope of the present study.

Reduction of iron ore

The reduction of iron ore by CO is a step-by-step procedure that starts with the conversion of hematite (Fe_2O_3) to magnetite (Fe_3O_4), followed by the transformation of wustite (FeO) to metallic iron. The above procedure is presented in the reactions below (eqs (1)–(3)).

$$3Fe_2O_3 + CO = 2Fe_3O_4 + CO_2$$
$$(\Delta G^0 = \Delta H - T\Delta S: -33096 - 54.04T), \quad (1)$$

$$Fe_2O_4 + CO = 3FeO + CO_2$$
$$(\Delta G^0 = \Delta H - T\Delta S: -29904 - 38.44T), \quad (2)$$

$$FeO + CO = Fe + CO_2$$
$$(\Delta G^0 = \Delta H - T\Delta S: -17598 - 21.56T). \quad (3)$$

It can also be evinced that the reduction of most of the Fe_2O_3 and Fe_3O_4 takes place in the temperature range 500°–600°C, following which the reduction of FeO commences in the temperature range 900°–1000°C where there is a high concentration of CO (the grey band/zone in Figure 2). This eventually establishes a dynamic equilibrium between FeO reduction and CO consumption, followed by Boudouard reaction, which is endothermic in nature, as presented below. At this stage, most of the iron oxide gets reduced to metallic iron, and the formation of the slag phase is evident in the tuyere region. The various stages of the reduction process and thermodynamic conditions can be evinced from the Fe–C–O stability diagram shown in Figure 2, which further suggests the concentration of CO required for the reduction of different ores[8]. For example, the concentration of CO

required for the reduction of Fe_2O_3 is less than 10%, while it is 20%–30% for Fe_3O_4 and 70% for FeO.

Formation of the slag phase

The formation of the slag phase takes place simultaneously with FeO reduction in the high-temperature combustion zone (i.e. the tuyere zone), where part of the unreduced FeO is expected to react with the impurities present in the iron ore and charcoal to form the slag phase. It is considered that during ancient smelting processes, the temperature did not reach the pre-defined melting point of iron (1537°C), and the final product in the furnace is expected to be a semi-solid, which is a mixture of metallic iron and the slag phase. This semi-solid mixture is difficult to separate. Therefore, sand or silica is often added to separate metallic iron from the slag phase and subsequently to form the fayalite phase ($FeSiO_2$), which has a melting point of about 1200°C (Figure 3)[9]. The formation of fayalite is evident from the analysis of entrapped slag found in the archaeological samples of iron objects from this region[10]. The melting point of the slag phase can decrease further due to the presence of limestone or calcium oxide to form the Kirsch-steinite ($CaFeSiO_4$) phase. The $CaFeSiO_4$ is then expected to react with $FeSiO_2$ to form a complex slag system known as Ca–Fe olivines, having a melting point around 1130°–1150°C (Figure 4)[11]. Some of the main sources of calcium oxide in the slag phase are impurities in iron ore and charcoal or added as a flux such as sand and limestone. The iron ore in this region contains high phosphorus that remains untreated in the metallic iron phase. However, iron artefacts from this region show a wide range of variation in phosphorus content from 570 to 2300 ppm (refs 10–12), indicating that some phosphorus removal has taken place in many of the ancient iron samples during the smelting process. Therefore, it can be construed from the above observations that the produced slag has high phosphorus capacity and calcium oxide, yielding Ca–Fe olivine slag that has a low melting point. The slag melting or softening temperature is important for the iron-making process since it acts as a thermal reserve zone and limits the maximum temperature of the process. The lower slag melting temperature makes the process more fuel-efficient, with better productivity and quality of the iron produced. Therefore, complex slags such as $FeSiO_2$ or Ca–Fe olivine begin to liquefy and subsequently flow downward, leaving behind the spongy iron. This product (spongy iron) is known as iron bloom. As the bloom iron is a product of solid-state reduction at low temperatures, it has small amounts of impurities. These iron blooms are further heated to red-hot temperature and skillfully hammered to obtain the desired shapes (i.e. ancient weapons).

Thermal energy and mass balance

Thermal energy balance

The combustion of charcoal takes place in the tuyere zone, or combustion zone, which has the highest temperature in the furnace. This value can be estimated by the adiabatic flame temperature (AFT) considering no heat loss to the surroundings[13]. The estimation of AFT does not consider heat loss through the refractory wall and various endothermic reactions such as decomposition of limestone, solution loss reaction and latent heat of melting. Therefore, AFT indicates the maximum temperature attained in the combustion zone of the furnace.

The metallic phase formed by reduction separates from the oxide phase or slag phase that does not have a fixed melting point. However, it has a definite temperature range for melting (i.e. between softening or melting temperature and complete melting temperature). Since slag melting involves a significant amount of heat absorption due to latent heat of melting, without much increase in temperature, it acts like a thermal reserve zone in the furnace, such that the temperature in the combustion zone is limited to a value slightly above the melting start or softening temperature of the slag.

Estimation of adiabatic flame temperature in the furnace

Several reactions are combined to describe the process and evaluate the heat and mass balance calculations, and the amount of nitrogen coming with oxygen during an air blow is also considered. The combustion of charcoal in the furnace can produce both CO_2 and CO. At high temperatures above 1000°C, almost 100% CO is produced (Figure 2). High-temperature gas formed due to the combustion of charcoal can supply heat energy to preheat the ore and reduce iron oxides. Material and heat balance for combustion and reduction of iron ore are given below.
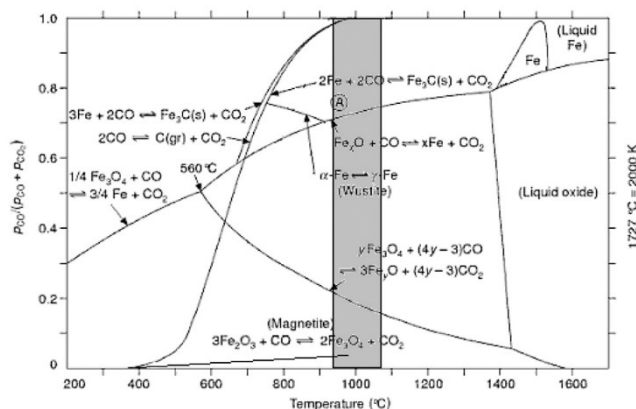

Figure 2. The Fe–O–C equilibrium diagram showing optimum conditions for the operation of the furnace[8].
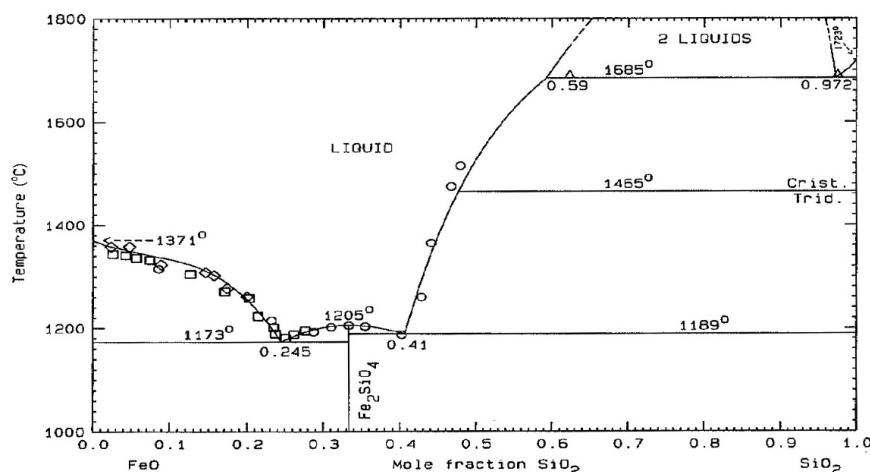
Figure 3. The FeO–SiO$_2$ phase diagram showing the formation of low melting fayalite (Fe$_2$SiO$_4$) phase (from Mukhopadhyay and Lindsley[11]).
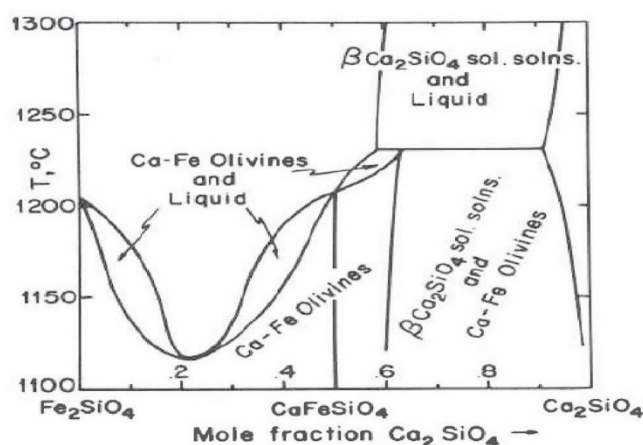

Figure 4. The CaSiO$_4$–FeSiO$_4$ system showing the formation of low-melting Ca–Fe olivines (from Ping et al.[9]).

Thermochemical data

- Considering no preheating, the initial gas temperature is 25°C or 298 K.
- AFT is indicated by T_f (°C).
- Thermochemical data, for specific heat (J/mol K) are as follows[14]:

$$C_{pCO} = 28.41 + 4.18 \times 10^{-3}T;$$

$$C_{pCO_2} = 44.14 + 9.04 \times 10^{-3}T;$$

$$C_{pN_2} = 27.87 + 4.18 \times 10^{-3}T;$$

$$C_{Fe} = 24.48 + 8.45 \times 10^{-3}T. \tag{4}$$

We can calculate T_f from the thermodynamic data, taking into account changes in enthalpy (ΔH) due to the overall reaction and specific heat (C_p) values of the product, where oxygen along with inert gas nitrogen in air have to be con-

sidered for heat balance. For the partial combustion of charcoal to CO we get:

$$\langle C \rangle + 0.5(O_2 + 3.76N_2) = CO + 1.88N_2,$$
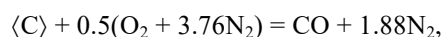
$$\Delta G = -111,700 - 88T \text{ (J/g mol)}.$$

From the heat balance, we can calculate T_f by solving eq. (5)

$$-\Delta H = 111,700 = \int_{298}^{T_f} (C_{pCO} + 1.88C_{pN_2})dT. \tag{5}$$

Using the above equation, we get $T_f = 1244°C$, which may not be sufficient for providing the extra heat energy for melting the slag phase. Therefore, we can consider some amount of CO$_2$ formation, which is more exothermic to provide the extra heat. Considering 90% CO and 10% CO$_2$ formation, and by combining the equations for CO and CO$_2$ formation we get

$$10\langle C \rangle + 5.5(O_2 + 3.76N_2) = 9CO + CO_2 + 20.68N_2,$$
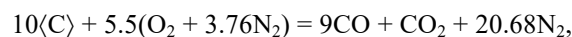
$$\Delta G = -1,400,940 - 793T \text{ (J/g mol)}.$$

This gives a much higher T_f value of around 1415°C. Therefore, the calculation shows that some amount of CO$_2$ formation is essential to provide the required thermal energy for the process.

Finally, we can combine the reactions of combustion of charcoal to 90% CO and 10% CO$_2$ gas to reduce iron ore from haematite to metallic iron, as shown in eq. (6).

$$10\langle C \rangle + Fe_2O_3 + 5.5(O_2 + 3.76N_2) = 2Fe + 6CO + 4CO_2 + 20.68N_2,$$
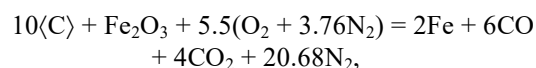
$$\Delta G = -1,510,940 - 795T \text{ (J/g mol)}. \tag{6}$$

The combined reaction of charcoal combustion and reduction of iron oxide helped estimate T_f at around 1345°C. Since this is lower than the melting temperature of iron, the product will be solid-state iron, which is porous due to the removal of oxygen and other impurities, such as slag, and can be designated as sponge iron. The slag is anticipated to be in a semi-solid state due to forming the low-melting slag phase such as FeO or complex olivine. T_f only indicates the maximum temperature that can be attained when there is no heat loss; however, in actual cases such as the Naikund furnace, once the slag melting or softening temperature is reached, heat absorption occurs due to the latent heat of melting, thereby restricting the temperature to slightly above the slag melting or softening temperature. Here, we have considered 10% CO_2 formation; however, with an increase in the amount of CO_2, T_f will also increase, which further indicates the high amount of melting of slag. Figure 5 is a schematic representation of the thermal profile inside the furnace involving the high-temperature tuyere zone or combustion zone.

Mass balance

The mass balance for reducing 1 g mol of iron is given by the Rist diagram (Figure 6)[15], over which the Fe–C–O phase stability diagram is superimposed to analyse the process methodically. The positive O/Fe in this diagram is from Fe_2O_3 reduction, while the negative O/Fe indicates the
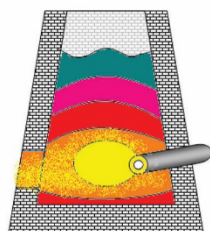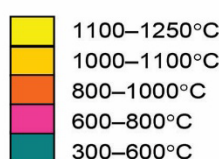

Figure 5. Schematic showing various temperature zones in the Naikund furnace (from Gogte[4]).
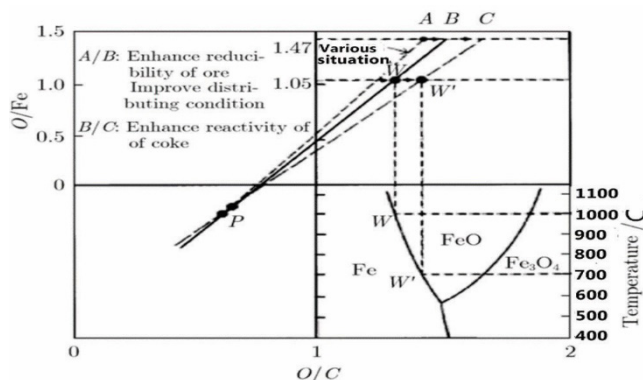

Figure 6. Rist diagram showing O/C ratio of the reducing gas versus O/Fe ratio of the reducing iron, with superimposed Fe–C–O stability diagram (from Rist and Bonnivard[15]).

incoming oxygen atoms from the blast. The efficiency of CO utilization is limited by the chemical pinch point W for FeO reduction. According to the prevailing conditions and thermodynamics, FeO reduction occurs when the CO/CO_2 ratio is 4 : 1 or more (i.e. CO is above 80% in the flue gas). The O/C ratio for 80% CO gas is estimated to be 1.2, from which the charcoal rate to produce 1 tonne of metallic iron can be estimated. The charcoal rate obtained from the Rist diagram analysis is the minimum value under the given conditions.

As the outlet gas composition of the Naikund furnace is unknown, we can only estimate the process by thermochemical analysis. The variation of flue gas composition in the furnace outlet is represented in Figure 6 by the three points, A, B and C. Considering the middle line with outlet composition B, which further represents the standard case we have studied, we can calculate the ratio for 6CO and $4CO_2$ at the outlet, which further suggests the O/C ratio as 1.4 (Figure 6). From this, we can also calculate the charcoal rate, considering 70% C in charcoal along with the remaining impurities and volatile matter. This further suggests the efficiency of the iron-extraction process as 70% and an estimated charcoal rate of about 2200 kg/tonne of iron produced. For case A, with a lower O/C ratio, we can consider 6CO and $3CO_2$ at the outlet, which further allows us to estimate O/C as 1.33 and a charcoal rate of about 2000 kg/tonne of iron. For case C, with a higher O/C ratio, we consider 50% CO at the outlet, i.e. 6CO and $6CO_2$, which gives an O/C of around 1.5 and charcoal rate of about 2700 kg/tonne of iron produced.

Concluding remarks

This study presents a thermochemical analysis of the megalithic iron-smelting process to demonstrate the ancient iron-making process at Naikund, Vidarbha region of India, around 900 BC. The important findings of the study are summarized below.

- The combustion of charcoal provides both thermal energy and reducing gas for the process. The Fe–C–O phase stability diagram shows that 80% CO or above is required for FeO reduction. However, adequate CO_2 formation is also essential for the high thermal energy requirement of the process.
- AFT for the combined reaction of charcoal combustion and reduction of Fe_2O_3 to metallic iron is estimated to be 1345°C, where the formation of solid-state porous iron (or sponge iron) can be evinced.
- Separation of the metallic iron and slag phase is necessary to produce the finished iron objects. Therefore, low-melting slag phase formation is essential to easily separate the slag and metallic phases. This is achieved by adding sand and limestone to produce the low-melting FeO and Fe–Ca olivine phases that have melting points
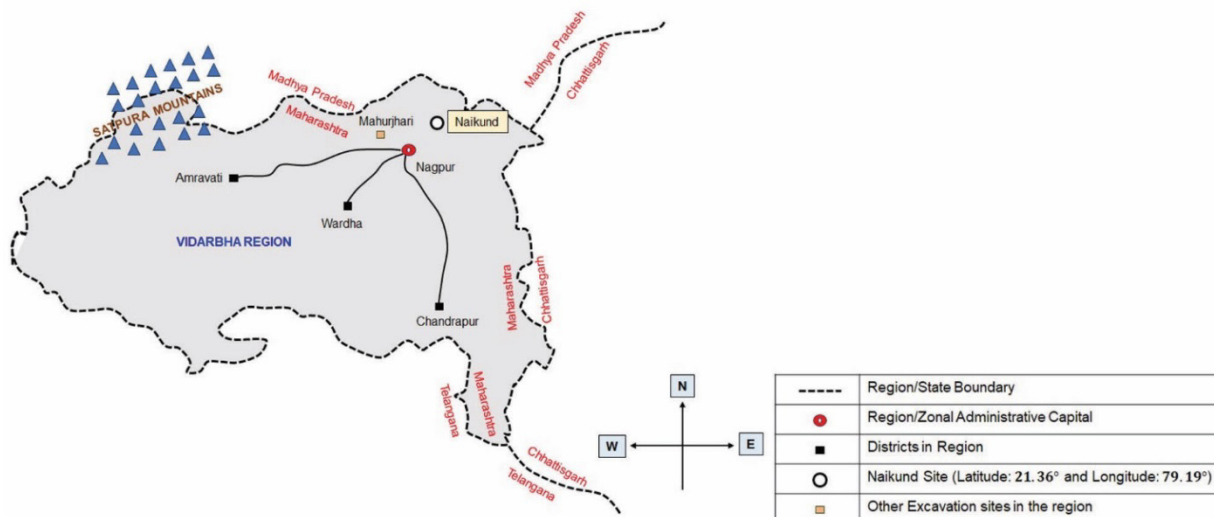
Annexure 1. Cartographic map showing the Naikund site near to Nagpur, Maharashtra, India (from Gogte[4]; lat. 21.36°, long. 79.19°). The site is marked as no. 53.

around 1205°C and 1140°C respectively. This is evident from the entrapped slag analysis and the presence of CaO in the slag as a major step for removing phosphorus from the ancient iron samples.

- The thermochemical and mass balance analyses performed with the Rist diagram superimposed over the Fe–C–O phase stability diagram indicate that 6CO and $6CO_2$ are the two outlet gases produced during the process with high O/C ratio (i.e. 15%), which further produce 2 g mol of metallic iron at a charcoal rate of 2700 kg/tonne of iron, demonstrating 70% efficiency of the metallic iron production process.

- The charcoal rate can vary based on different process parameters. For example, for a lower O/C ratio (1.33%), 6CO and $3CO_2$ yield a charcoal rate of 2000 kg/tonne of iron.

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