

Chapter 2

From Ores to Metals

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Introduction

Archaeometallurgy is one of the most interdisciplinary of all branches of historical inquiry. Disciplines that contribute essential insights into archaeometallurgy include archaeology, ethnoarchaeology, economic history, the history of technology, the history of philosophy (beliefs about transformations of matter), philology, social anthropology, mineralogy, petrology, geochemistry, economic geology, extractive metallurgy, physical metallurgy, foundry practice, blacksmithing and goldsmithing, ceramic technology, numismatics, forestry, and limnology.

No single person can be an expert in all of these fields, and few among us can hope to become even competent in more than three or four of them. All students of past mining and metallurgy must therefore rely upon the expertise of others, so archaeometallurgical projects are best carried out by teams of collaborating specialists. However, some forms of expertise are in very short supply in archaeometallurgy. One underrepresented perspective is that of economic geology, which is the study of how useful elements (mostly metals) are concentrated by geological processes to form ores and ore deposits. It may seem surprising that expertise in economic geology should be hard for archaeometallurgists to find, given that industrial societies are absolutely dependent upon the metals and minerals produced from ore deposits. This situation reflects the decline of interest in the subject within academic geology over the last 25 years. Few doctoral dissertations are now written in economic geology, and it is hard even to get well-qualified candidates to apply for the few university lectureships that are advertised in this field, given the great difference in the salaries offered by universities and mining companies.

My aims in this chapter are: (1) to provide a very brief introduction to the subject and its major findings; (2) to summarize the methods used to study ore minerals and their associations; and (3) to show how some knowledge of the properties and

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distribution of ore minerals can help us understand the prehistory of extractive metallurgy (smelting).

What are Ores?

A useful starting point is the definition provided in a standard textbook: “(o)res are rocks or minerals that can be mined, processed and delivered to the marketplace or to technology at a profit” (Guilbert and Park 1986, p. 1). A large volume of ore is termed an ore deposit. For the purposes of archaeometallurgy, we need to detach this definition from the modern context of commodity markets, which have existed for only about 200 of the 10,000 years since humans first used metals. It is important, however, to retain the idea that the classification of a given volume of rock as an ore deposit is a relative judgment. Today what determines whether a volume of rock is an ore are: (1) the market price of the metal that it contains and (2) the cost of obtaining it from the ore and moving it to market. Before the modern era, the factors that determined whether a given rock or alluvial sediment was an ore were: (a) whether the metal(s) it contained were considered valuable and (b) the technologies available for mining, concentrating, and smelting the metal(s).

My first restriction of the definition requires explanation. Today, every element in the periodic table has its price, but this was obviously not so in the remote past. Many elements were not isolated as pure substances and named until the nineteenth or twentieth century. Even metals that were known in prehistory did not necessarily have value at all times and places. Gold offers a good example. Alluvial gold (concentrated in alluvial deposits because of its high specific gravity) occurs on all continents, and mobile populations (e.g., hunter-gatherers and pastoralists) were surely aware of its existence. Yet there is little evidence that it was even collected as a curiosity before about 4500 BCE. From this point on, gold became highly valued throughout Eurasia, beginning around the Black Sea (Chernykh 1992; see Kienlin; Yener and Lehner; Courcier, this volume). The use of gold also emerged, independently of the Old World, in parts of South America, Central America, and the Caribbean, beginning around 2000 BCE (Aldenderfer et al. 2008; see Hosler; Lechtman, this volume). However, there is no evidence of its use in sub-Saharan Africa (except in Nubia and areas adjacent to the Red Sea) until portions of the subcontinent were incorporated into Muslim trading networks after 750 CE (Killick, this volume). Nor was gold used in North America before the sixteenth century CE, or in Australia before the eighteenth century; in both these regions the first extraction of gold was by European colonists.

The point here is that metals do not have intrinsic value. Value is ascribed to metals by people, and their judgments of what was valuable, and what was not, varied widely through time and space. Thus, what we count as an ore today was not necessarily an ore in the remote past. Another very striking example of this is seen in some Bronze Age mines in Wales (Cwmystwyth, Great Orme, and Nantyreira) where the copper minerals were removed, but rich veins of the lead mineral galena

(PbS) were not (Ixer 1999; Timberlake 2003). Lead was not valued, so lead veins were not ores at that time.

My second restriction on the archaeometallurgical definition of ore resources reflects the fact that with technological advances the “cutoff” in metal content that makes a rock an ore declines. Thus, many mining districts have been mined over and over again, with each new period of mining attributable to an advance in technology. For an extended example, let us consider copper. Although we have, as yet, little direct evidence of the grade of ore used by the earliest copper smelters in the early fifth millennium BCE, it seems likely that the first crucible smelting technology would have required nearly pure hydroxycarbonate ores (malachite and azurite), which contain about 60 % copper by mass. If we fast-forward to the present, the huge open-pit copper mine at Sierrita, Arizona—about 40 km from where this article is written—is mining rock that contains, on average, only 0.25 % copper and some molybdenum. For this mine to be profitable at present world prices, at least 200,000 tons of rock must be mined and milled every day.

Advances in both the factors of production (the technologies of mining, extractive metallurgy, and transportation) and the organization of production (labor skills and coordination, finance, and marketing) have allowed the expansion of the term “ore deposit” to rocks of steadily declining metal content. Sierrita is one of several dozen gigantic open-pit mines that today produce most of the world’s copper from very low-grade porphyry copper deposits (Guilbert and Park 1986; Robb 2005). These are thought to contain more than 85 % of all the copper in the earth’s crust that can be considered ore under present and projected technological, economic, and social constraints. The change from underground to open-pit mining in the early twentieth century reflected the exhaustion of richer copper ore deposits; Gordon et al. (2006) estimate that 97.5 % of the 400 million metric tons of copper that have ever been extracted were mined since 1900. This represents about 26 % of the metal in all copper ore deposits that have been discovered so far in the earth’s crust. Since the amount of copper extracted per year is growing much faster than the amount added by the discovery of new copper deposits (Gordon et al. 2006, Fig. 4), it appears likely that within a century we will be unable to add newly mined copper to the stocks already in use. This is because the amounts of energy and water required to process the exponentially larger volumes of rock with copper contents below about 1000 ppm will be prohibitive.

An important consequence of this trend for archaeometallurgy is that many of the copper mines used in antiquity have already been destroyed. We cannot assume that those mines that have escaped destruction, however impressive, were the major sources used in prehistory. This point is well illustrated by the case of the impressive ancient mine at Rudna Glava, Serbia, which was once assumed to have been the major source for Eneolithic copper artifacts in that region of the Balkans. Yet lead isotopic analysis of a substantial sample of Eneolithic copper artifacts from the Balkans (Pernicka et al. 1993; Radivojević et al. 2010) showed that none of them derived from Rudna Glava ores. The search for ancient mines in alluvial ore deposits is a particularly fruitless task, for these have been repeatedly worked and reworked with advances in the technology for recovering ore from them. Artifacts dating as

far back as the Bronze Age have been recovered over the last four centuries from alluvial tin gravels in southwest England (Penhallurick 1986), but no ancient mine has yet been found in these deposits. Nor should we expect to find a prehistoric mine in the alluvial goldfields of West Africa, which are known from historical documents to have been major sources of gold for the Muslim world (Levtzion and Hopkins 2000).

In other words, the ore resources of the world that we live in are very different from those that existed in prehistory. Most of our evidence for the types of ores used in the distant past, and how these were processed, must therefore come directly from examination of ore samples recovered from prehistoric smelting sites. However, the study of ores is the least developed part of archaeometallurgy, and the literature is full of poorly informed speculation about the ores used in the past (Ixer 1999). The main purpose of this chapter is therefore to introduce the topic and to plead for the training of more specialists in archaeological applications of ore geology. It will also show how the history of extractive metallurgy—the sequence in which the various metals were won from their ores—reflects the geological processes that formed ores, the chemical properties of particular ore minerals, and the slow growth of human understanding of these properties.

The Relative Abundance of the Metals in the Crust of the Earth

Ores contain, in all cases, a much higher concentration of the metal than the average concentration of that metal in the earth's crust. Geochemists have estimated the crustal abundance of the elements by: (1) calculating, from chemical analyses in the literature, the average composition of each of the major types of rock in the crust and (2) multiplying these averages by the estimated mass fraction of each of these rock types in the crust, as inferred from surface outcrop, boreholes, and remote sensing (magnetic and gravity surveys and seismic probes).

Estimates of average abundances of the major metals of industrial interest (extracted from Tables A.10 and A.11 in Faure 1991) are listed in Table 2.1. Looking at the first column (abundances averaged across the Earth's crust), we see that:

- (1) aluminum, iron, magnesium, and titanium are geochemically abundant (>0.5 mass%) and thus will not be exhausted at any plausible level of demand;
- (2) manganese, vanadium, chromium, and nickel are present above 100 ppm;
- (3) all other metals are geochemically scarce (<100 ppm); and
- (4) the precious metals (silver, gold, and platinum-group elements—PGEs) and mercury are ultra-trace elements (<0.1 ppm).

Slightly different values can be found in other texts (e.g., Krauskopf and Bird 1995) and reflect different assumptions about the mass fraction of the various rock types in the Earth's crust, but the rank order for the abundance of the metals is the same in each case.

Table 2.1 Estimated abundance by mass of selected metals in the earth's crust and in major rock types. Abundances in ppm except for Al, Fe, and Mg, which are in percent. (Adapted from Faure 1991, Tables A.10 and A.11)

	Crystal average	Ultramafic rocks	Basalt	High-Ca Granite	Low-Ca Granite	Shale	Sandstone	Carbonate rocks	Deep-sea clays
Al (%)	8.40	1.20	8.28	8.20	7.20	8.00	2.50	0.42	8.40
Fe (%)	7.06	9.64	8.60	2.96	1.42	4.72	0.98	0.33	6.50
Mg (%)	3.20	23.20	4.54	0.94	0.16	1.50	0.70	4.70	2.10
Ti	5,300	300	11,400	3,400	1,200	4,600	1,500	400	4,600
Mn	1,400	1,560	1,750	540	390	850	#	1,100	6,700
V	230	400	225	88	44	130	20	20	120
Cr	185	1,800	185	22	4	90	35	11	90
Ni	105	2,000	145	15	4.5	68	2	20	225
Zn	80	40	118	60	39	95	16	20	165
Cu	75	50	94	30	10	45	#	4	250
Co	29	175	47	7	1	19	0.3	0.1	74
Pb	8	0.5	7	15	19	20	7	9	80
Sn	2.5	0.5	1.5	1.5	3	6	0.1	0.1	1.5
W	1.0	0.5	0.9	1.3	2.2	1.8	1.5	0.6	1.0
As	1.0	0.8	2.2	1.9	1.5	13	1.0	1.0	13
Sb	0.2	0.1	0.6	0.2	0.2	1.5	0.01	0.2	1.0
Hg	0.09	0.01	0.09	0.08	0.08	0.40	0.03	0.04	0.10
Ag	0.08	0.05	0.11	0.05	0.037	0.07	0.01	0.01	0.11
Au	0.003	0.006	0.004	0.004	0.004	#	#	#	#

Insufficient data for calculation of mean abundance

Archaeometallurgists should immediately spot the paradoxes in this column. Why were the first metals to be used (copper, lead, and gold) among the scarcest? Why were six of the seven most abundant metals not used before the last two centuries? Keep these questions in mind, as we will return to them later in the chapter.

The other columns in this table show that some metals are more abundant in some types of rock than in others. The most extreme differences are for magnesium, cobalt, nickel, and chromium, which are concentrated in ultrabasic rocks (dunites, peridotites, etc.). Conversely, lead is found at higher concentrations in granitic rocks and in clays than in ultrabasic or basic rocks (gabbros and basalts). For some metals—manganese, copper, lead, zinc, and arsenic—the highest values are seen in marine clays. These elements tend to oxidize at the Earth's surface to form compounds that are soluble in water and thus are carried to the ocean. There they are adsorbed on the surfaces of clay particles and sink slowly to the ocean floor.

In no case, however, are the concentrations listed in Table 2.1 high enough for the average rock or sediment to be considered an ore under present or projected technological and market constraints. Ore deposits are often formed where subsurface geological processes have removed metals from common rock or from masses of molten magma, and have redeposited them in other locations at much higher concentrations. Alternatively, ore deposits are formed where surface processes have eroded minerals from rocks and concentrated them elsewhere. The degree of concentration above the values in the parent rock is called the *enrichment factor*. In the case of

the Sierrita porphyry copper deposit, the parent rock is a low-calcium granite. If we assume this to have a typical copper concentration (from Table 2.1) of 10 ppm, then the enrichment factor for the ore body as a whole (0.25 % Cu) is about 250 times (250 ×). A piece of pure malachite (60 % Cu) within this ore body has a local enrichment factor of 60,000x. The highest known enrichment values are at the Almaden mercury mines of Spain (Silurian to Devonian age), where some ore bodies contain as much as 25 % mercury. The Almaden deposits have yielded about a third of all mercury ever mined, much of which was used to extract silver from Mexico and Peru during the Spanish colonial era. Geochemical research (Higuera et al. 2000) suggests that this mercury derived ultimately from basaltic magmas, which typically contain only 0.09 ppm Hg (Table 2.1). The enrichment factor for the richer mercury deposits at Almaden may therefore be as high as 2.8×10^6 x.

How do Ore Deposits Form?

Ore deposits represent the most extreme examples of the chemical differentiation of the earth over the last 4.5 billion years. Slow cooling over this time converted an initial mass of relatively homogeneous superheated gas into a planet with a metallic (iron–nickel) core, a mantle of ultrabasic composition (mostly liquid with a viscous outer zone), and a thin, brittle, and highly differentiated crust. The major question addressed by academic geochemists is how the different rocks listed in Table 2.1 (and the many variants not listed) could all be produced from parent rocks that had the ultrabasic composition of the upper mantle. My discussion is restricted to the formation of ore deposits and is drawn largely from Guilbert and Park (1986), Ixer (1990), Robb (2005), and Dill (2010). Space does not permit the inclusion of diagrams to illustrate these processes; for these the reader should consult Robb (2005).

Ore Deposits Associated With Igneous Rocks

One way to form rocks of different chemical compositions from a molten magma is through *fractional crystallization*. Iron, chromium, titanium, and vanadium oxides and iron/magnesium silicates and aluminosilicates (olivines and pyroxenes) are the first minerals to crystallize from ultrabasic magmas. If these separate by settling under gravity, the remaining liquid will be relatively enriched in other elements, such as the alkalis, the rare earths, and some metals. The residual liquid will also contain more silicon, aluminum, water, and carbon dioxide than the crystal mush. Thus, the chemical composition of the residual melt will move towards those of the more silica-rich intermediate rocks (e.g., andesite).

The early-forming crystalline minerals in a magma chamber have different densities and may separate by gravitational settling to produce a layered suite of rocks.

Almost pure layers of magnetite (Fe_3O_4) ore—with or without ilmenite (FeTiO_3)—and chromite (FeCr_2O_4) occur in many ultrabasic igneous suites. Most of the exploitable world reserves of the PGEs are in a single chromite-rich layer in South Africa (the Merensky Reef) that is only 30–90 cm thick. The Merensky Reef formed within the largest known layered igneous intrusion, the Bushveld Igneous Complex (BIC), which goes from ultrabasic rocks at the bottom to acid rocks (rhyolites and granites) at the top. Chromium, iron, platinum, vanadium, and titanium ores are restricted to the ultrabasic and basic layers, while copper and tin mineralization is associated with the late-forming acid rocks at the top of the sequence. The sequence reflects typical changes in the compositions of magmas that are produced by fractional crystallization.

Most ore deposits associated with igneous rocks are however generated through the “conveyor-belt” mechanism of *plate tectonics*. At subduction zones, which are most commonly where oceanic crust is pushed against a continental plate, the denser, thinner basaltic crust is forced down beneath the continents. At depths of 60–170 km, the subducted plate melts to generate a magma. This magma has two significant features for ore formation: (1) The subducted plate has a veneer of sediment that (as shown in Table 2.1) carries relatively high concentrations of many metals, and (2) it has a higher water content than is typical of the upper mantle, due both to the sediment veneer and to reactions between basalt and seawater at the ocean floor. The resulting magma is buoyant and thus rises slowly through the upper mantle and overlying crust, or absorbs portions of crust to produce magmas of andesitic composition. Alternatively, the magma may transfer its heat to crustal rocks, which may melt in turn to form intermediate-to-acid magmas. Many of these magmas erupt at the surface as chains of volcanoes parallel to the subduction zone, forming either mountain chains (e.g., the Andes) if the melting occurs under continental crust, or island arcs (e.g., Indonesia) if the subduction zone lies offshore under continental margins. Some magmas solidify as plutons below the surface, and the reactions that occur with crustal rocks around these plutons generate important classes of ore deposits, including the porphyry copper and molybdenum deposits.

Elements that cannot be accommodated in the crystal lattices of the early-forming minerals concentrate in residual fluids due to fractional crystallization of these magmas. The most important such elements in ore genesis are hydrogen, carbon, sulfur, chlorine, and fluorine (as water and HCO_3^- , HS^- , SO_4^- , Cl^- , and F^- anions). These form hot brines and molten sulphides that effectively scavenge and transport metal ions from the original magma and from the crustal rocks through which the ascending fluids pass. Once almost all the magma has crystallized, many metals (Cu, Mo, Pb, Zn, Au, and Ag) can be concentrated in these fluids at several orders of magnitude above their original abundance in the magma. The amount of water in the magma and the degree of oxidation are thought to largely determine which metals are concentrated. The magmas that produce porphyry copper deposits are thought to have contained less water than those that produce the porphyry molybdenum deposits. Large volumes of fluids were certainly required to form ore deposits of the most *incompatible* metals, which are not readily accepted in the crystal structures of most rock-forming minerals. Incompatible metals (e.g., Sn and W) are geochemically very

scarce (Table 2.1) and thus must be scavenged from large volumes of magma or rock by large volumes of fluids. Ores of these metals and of other incompatible elements (B, Be, Li, Cs, Nb, and Ta) are typically found at the very top of granitic plutons and in pegmatites.

All that remains to form ore deposits is to precipitate these metals from solution. Cooling lowers the solubility of metals in hot brines, as does the decrease of pressure near the earth's surface. These changes suffice to produce relatively low-grade ore deposits formed around the margins of large igneous intrusions, as in the porphyry copper deposits, which generally contain less than 2 mass% copper (Guilbert and Park 1986). The hot aqueous solutions typically spread out from the igneous intrusion into the enclosing host rocks and react with them, a process called *metasomatism*. For example, skarns are formed by metasomatism of limestones or dolomites and are important hosts worldwide for ore deposits of W, Sn, Mo, Cu, Pb, and Zn.

The average concentrations of metals in these deposits, though orders of magnitude above average concentrations in the crust, are too low to have been ores for early metallurgists. Patches of much higher grade can however form in suitable traps. These are generally joints and cracks in igneous or metamorphic rocks, or bedding planes in sedimentary rocks, which become filled with metallic minerals and associated *gangue minerals* (i.e., those without economic value) such as quartz, pyrite, carbonates, tourmaline, etc. These minerals are precipitated from brines and molten sulphides forced through these channels, which gradually fill to form veins and narrow sheets that can be very rich in metal content. These were the most important sources of copper, lead, zinc, silver, and tin before the era of open-pit mining. Quartz veins above igneous intrusions were important sources of gold in many areas—most of the gold exported from Great Zimbabwe and its successor states, for example, derived from the mining of quartz veins (Summers 1969). Most gold-bearing veins date to the Archean period (3000–2500 Ma), quite early in the evolution of the earth.

Hydrothermal Deposits: Ore Formation by Interaction of Surface Waters With Subsurface Magmas and Rocks

Since the earth's crust is solid, it encloses a fixed volume. Thus, any volume of plate subducted into the mantle must be balanced by an equal volume that is forced up into or through the crust. Most of this extruded material appears at *seafloor spreading centers*, which are linear volcanoes that build the basaltic seafloor. An important class of ores is formed here as seawater seeps down through the seabed along cracks initiated by the pressure of the underlying magma. These large volumes of water are heated, extract metals from the basaltic magma, and are expelled back through “black smoker” vents into the cold ocean, where metal sulphides (Cu, Zn, and Ni) immediately precipitate to form ores. These are called *volcanogenic massive Sulphide* (VMS) deposits. Most of these deposits have probably been destroyed by subduction, but some were fortuitously preserved when slabs of former ocean floor were torn off and thrust up over continental crust. These are known as ophiolite

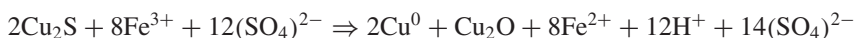
complexes. Two ophiolites—those of Oman and Cyprus—were extremely important ore sources for the Bronze Ages of Mesopotamia and the eastern Mediterranean, respectively (Hauptmann 1985; Stos-Gale et al 1997). Other historically important VMS deposits include the Rio Tinto Cu–Ag–Au mine in Spain and the Kuroko “black ore” Cu–Zn–Pb in Japan (though these may have formed at island arcs rather than at subduction zones).

A related class of massive sulphide deposits are the *sedimentary exhalative* (SEDEX) deposits, which contain about half of the known Pb and Zn ore reserves. These formed in relatively shallow waters (as in the Red Sea today) where major faults allow brines to descend deep below the surface and to return as hot solutions laden with metals, which precipitate as soon as they meet cool sea or lake waters.

VMS and SEDEX ore deposits are *syngenetic*, meaning that the ores were deposited at the same time as the sediments that host them. However, ore deposits can also form in sedimentary rocks by *epigenetic* mineralization, meaning that the metal ions originated elsewhere and entered the sediments long after the latter were deposited. These metals were introduced in low-temperature (<150 °C) brines that moved through pore spaces and were precipitated by reaction with carbonates or by reduction by organic matter in sediments.¹ The Zambian/Katangan Copperbelt, the central European Kupferschiefer, and the Mississippi Valley Pb–Zn deposits are examples of epigenetic hydrothermal deposits.

For archaeometallurgists, a particularly important case of interaction of surface waters with metal-bearing rocks is that which occurs where copper sulphide ore deposits of igneous origin encounter surface waters and oxygen. The primary (*hypogene*) ore minerals in these deposits are mostly sulphides of copper and iron, particularly pyrite (FeS₂) and chalcopyrite (CuFeS₂). These are oxidized by exposure to oxygenated surface waters to form carbonates, oxides, and hydroxides. Some iron remains at the surface as relatively insoluble oxides and hydroxides, which give a strong red color to the top few meters (known as *gossan* or *iron hat*) of the oxidized zone (Fig. 2.1). Some copper is retained within the oxidized zone, mostly as cuprite (Cu₂O, red), malachite (Cu₂CO₃(OH)₂, green), and azurite (Cu₃(CO₃)₂(OH)₂, blue). On present knowledge, these attractively colored minerals were first used for personal ornaments in the Middle East from the late 11th millennium BCE, preceding the development of agriculture by two millennia. They became widely distributed in Iran and the Levant in the eighth to ninth millennia, and were probably transported there with obsidian from Anatolia (Schoop 1995; Thornton 2002).

Native copper is formed in the oxidizing zone by the reaction:



(Guilbert and Park 1986, Eq. 17.19).

Although native copper is very often noted in the oxidized zone, this does not necessarily mean that in any given deposit it occurred in pieces large enough to

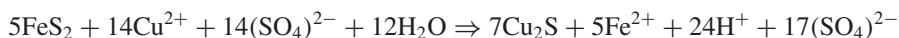
¹ The temperatures of formation of ore deposits are largely inferred from the study of tiny fluid inclusions trapped within the solid minerals—see Guilbert and Park (1986: 252–260).



Fig. 2.1 The thin red layer is the gossan over the copper sulphide ore deposit at Bisbee, Arizona. The rock beneath this shows the typically bleached appearance of the supergene layer above the water table. The zone of supergene enrichment begins about 50 m below the level of the road. (Photograph by author)

be exploited. There has been much fruitless argument in archaeometallurgy about whether the use of native copper (forged but not melted) was a universal stage in western Eurasia before the development of smelting. Wertime (1973), Charles (1980), and Amzallag (2009) all assert that it was, but evidence for the use of native copper in western Eurasia is as yet surprisingly rare (Thornton et al. 2010). Whether this absence is apparent or real is hard to judge, as the chemical composition of the earliest copper is not necessarily a good clue. Although native copper is generally very pure (Rapp et al. 2000), there is no good reason to suppose that copper reduced in crucibles from masses of cuprite, malachite, or azurite in the oxidized zone would be any less pure. Metallographic examination is often more conclusive, but has rarely been applied to the earliest metals in Eurasia—the excellent work of Stech (1990) on the native copper industry of Çayönü in Anatolia (late ninth millennium BCE) is a notable exception. Finds of partially worked native copper are the best evidence but have rarely been noted in the Old World and never (so far) in South America. The contrast with North America, where there is abundant archaeological evidence for working of native copper, is very striking (see Ehrhardt, this volume). The direct forging of native copper began here around 4500 BCE (Martin 1999) and it remained the only metallurgical technology in North America (except for very rare instances of the forging of iron meteorites and native iron) until colonization by Europeans (Wayman et al. 1992).

Oxidation of the pyrite (FeS_2) in the oxidized zone produces sulfuric acid and ferrous sulfate. These acidic solutions leach copper from the oxidized zone down to the water table, where copper is precipitated, mostly as chalcocite replacing pyrite at the top of the original hypogene ore zone:



(Guilbert and Park 1986, Eq. 17–39).

The excess acid is neutralized by reaction with gangue minerals and by slightly alkaline ground waters. This reaction produces a zone of *supergene enrichment*, with copper concentrations much higher than in the primary (*hypogene*) ore beneath it, and vastly greater than in the oxidized and leached zone above. Many copper mines today, such as the vast open-pit mine at Morenci in eastern Arizona, are only economically viable because of supergene enrichment.

Supergene enrichment is noted on all types of copper deposit, but its significance for prehistoric metallurgy varies with location. On stable continental surfaces, the enriched layer may be buried under a hundred meters or more of oxidized and leached overburden (as in Fig. 2.1) and thus would only be accessible to early metallurgists if exposed by erosion. In northern latitudes, much of the oxidized layer may have been scraped away by the advance of glaciers, bringing the enriched supergene sulphides, or even the hypogene ore, close to the surface (as in the Austrian Alps). In very arid areas, such as the Atacama Desert of Chile, the oxidized layer may retain, and even concentrate, much of the copper in the form of soluble sulfates and chlorides that in more humid climates would have been flushed down the profile. The point here is that copper deposits vary widely in their character. Thus, the simplified general model of a copper ore deposit used by many archaeometallurgists (after Charles 1980) is no substitute for a careful reading of the geological literature on the ore deposits of the region under investigation.

Ore Formation by Sedimentary Processes

As noted above, high-grade iron ores are often formed by settling in magma chambers to form magnetite layers, but for technological reasons (see below) these ores were rarely utilized before the development of blast furnaces. Iron smelters in earlier times preferred iron oxide ores formed by sedimentary processes. (Iron sulphides are abundant but have never been used as iron ores because even small amounts of intergranular iron sulphide cause iron to crumble when hot-forged.) Very large deposits of iron oxides were formed as *chemical sediments* (i.e., precipitated from aqueous solution) during three distinct periods of the earth's development—two in the Archean (3500–3000 and 2500–2000 Ma) and one in the Proterozoic (1000–500 Ma)—to form the ores known as banded iron formations (BIFs). These have layers of iron oxide (magnetite or hematite) or iron carbonate (siderite) alternating with silica-rich layers (usually chert). They are thought to have formed when periodic pulses of

deep water containing Fe^{2+} ions were raised by upwelling along continental margins and converted to the less soluble Fe^{3+} by oxygenated surface waters. The silica-rich layers apparently derived by precipitation of dissolved silica, but after the evolution of marine creatures (diatoms) that built their skeletons of silica, there was no longer enough silica in solution to precipitate chert layers, so no BIF formed after this time (Robb 2005).

Although BIFs supply much of the world's iron today, there is little evidence for their use in prehistory, probably because: (1) they are mostly found in areas where iron was not smelted until European colonization (Australia and North America) and (2) they tend to be very hard, and thus laborious to mine by hand unless heavily weathered to iron hydroxides, as in Madagascar, where they were smelted in prehistoric times (Gabler 2005). The earthier and softer hematite and limonite (iron hydroxide) ores, such as the Jurassic ores of Alsace-Lorraine, were preferred in northern latitudes. These types of ore formed in shallow waters, often by chemical replacement of carbonates. In northern latitudes, *bog iron* ores were often the preferred source for small-scale iron smelting in prehistory. The presence of peat produces acid waters that can carry iron in solution, often as complexes with humic acids. These compounds are broken down in ponds by bacterial action, precipitating the iron as the hydroxides goethite and lepidocrocite (collectively called limonite). Bog ores are small but renewable resources (Ixer 1990), and these ores are easily smelted. Spring deposits of limonite also made suitable ores in some locations.

In the tropical zones of sub-Saharan Africa, Brazil, and Southeast Asia, the most widely available iron ores are *laterites*. These have formed over the last 100 million years on stable continental platforms (cratons) that are subjected to alternating very wet and very dry seasons. Under these conditions, all elements in the soil except the relatively insoluble iron and aluminum tend to dissolve and be leached away (Delvigne 1998). Iron and aluminum ions are slowly moved downwards during the rains but reprecipitate as oxides and hydroxides between the high and low annual levels of the water table during the dry season. Iron-rich laterites form over ultrabasic and basic rocks, and aluminum-rich bauxites form over acid rocks. While laterites are generally of relatively low grade, usually containing residual quartz and clay minerals, they are widely available. The largest known concentration of prehistoric bloomery iron smelting furnaces—34,683 in a 30-km stretch along the Senegal River in Mauritania—used low-grade ores from laterites (Robert-Chaleix and Sognane 1983; Killick 2013). Laterites that formed over ultrabasic rocks may also contain significant amounts of nickel, cobalt, and chromium. While chromium would not be reduced in small hand-blown furnaces (see below), nickel and cobalt would pass into the iron. Thus, prehistoric iron–nickel alloys cannot automatically be assumed to have derived from the forging of meteorites (as many archaeometallurgists have suggested).

Gold and the PGEs have much higher specific gravities than most rock-forming minerals and are not dissolved by most surface waters. When ores of these elements are eroded, the metal grains may be carried into streams, where the loose sediments are sorted by flowing water according to specific gravity and grain size. Concentrations of metals formed in this way are termed *placers*. Few (if any) large placer gold

deposits remain today, but all historical “gold rushes” began with the discovery of placer gold. The earliest prehistoric “gold rush,” which began around the western and northern shores of the Black Sea in the mid-fifth millennium BC and lasted about a thousand years, also exploited placer gold (Chernykh 1992; Kienlin, this volume). Inclusions of PGEs in gold suggest that the gold came from a placer deposit, since gold and PGEs are not usually found in the same primary ores. Hard PGE inclusions are pressed into soft gold flakes by tumbling in streams.

Heavy minerals that are chemically stable in surface waters also form placers. The most important of these for archaeometallurgists is cassiterite (SnO_2), the principal ore mineral of tin. Depressingly little work has been done on the early mining and metallurgy of tin, so it is not known whether tin for the earliest bronze of western Eurasia derived initially from placers, though this seems very likely. Tin/tungsten placers derived from the granite batholiths of Cornwall and Devon have been repeatedly worked and reworked since the Bronze Age (Penhallurick 1986), but are now exhausted, as are most terrestrial tin placers throughout the world. (The huge tin placers of Malaysia, the world’s largest producer of tin, are almost entirely offshore.) It appears from studies in Cornwall and Devon (Tylecote et al. 1989; Malham et al. 2002) and in South Africa (Chirikure et al. 2010) that placer tin production can sometimes be distinguished from mined tin by the chemical composition of the slags produced from smelting the concentrates. This is because heavy minerals like ilmenite (FeTiO_3) and zircon (ZrSiO_4), which are not generally present in tin ores but have eroded from other rocks in the region, may be concentrated with cassiterite in the placers. These dissolve in the slags to give higher Ti and Zr concentrations than occur in slags produced from mined ores (Chirikure et al. 2010).

Methods for Studying Ores Recovered From Archaeological Contexts

Many of the ore deposits used by early miners and metallurgists no longer exist, although the astonishing discovery of unknown Bronze Age mines in Britain during the 1990s (Timberlake 2003) shows that we should never assume that none remain in a given region. Archaeometallurgists have generally tried to infer which ores were used by indirect means. One approach has been to look for clues in the chemical composition of the metals and slags recovered from archaeological sites; the other has been to look at the distribution of ore deposits on a very broad regional scale. Only in the German-speaking countries, where the study of ores with the microscope was first developed, has the systematic examination of the ore minerals recovered from archaeological sites been a consistent component of archaeometallurgical projects. Much of the publication of this research has been undertaken by the Deutsches Bergbau-Museum in Bochum, which currently lists some 165 monographs on the prehistory and history of mining and metallurgy. In Anglophone archaeometallurgy, only Robert Ixer, George (Rip) Rapp, and Alan Craig have done systematic work on ores (e.g., Ixer and Patrick 2003; Rapp et al. 1990, 2000; Craig and West 1994),

while in France, David Bourgarit, Benoit Mille, and their students have recently made major contributions (see references in Bourgarit 2007). In large part, this reflects the fact that English- and French-speaking archaeometallurgists usually have their primary training in physical metallurgy, while German-speaking archaeometallurgists have theirs in geology and geochemistry. Important recent contributions have also been made by the Iranian geologists Nima Nezafati and Morteza Momenzadeh, in collaboration with German archaeometallurgists (e.g., Nezafati et al. 2008).

Over the last century, economic geologists have used a number of methods to infer the large-scale processes that create ore deposits. These include field observation, the methods of structural geology, the optical microscope, and (since the 1960s) the scanning electron microscope, electron microprobe, and isotopic ratio measurements to identify characteristic associations of ore minerals in particular settings. Archaeometallurgists use many of these same techniques to study ores from archaeological sites, and to trace archaeological ore samples to the ore deposits described for the region in the geological and mining literatures. Studies of ores samples may also be useful in reconstructing how ores were treated before they were smelted. I will concentrate here on the use of optical and electron microscopes to identify minerals and document ore associations and textures; on the use of the electron microprobe and micro-X-ray fluorescence (μ -XRF) for chemical analysis; and on X-ray diffraction and Raman spectroscopy for mineral identification.²

Optical Microscopy

As most ore minerals are opaque in standard 30-micron-thin sections, classical ore microscopy centered on the examination of polished blocks with vertical reflected light. Ore microscopy was largely developed in the USA (e.g., Campbell 1906; Murdoch 1916) and in Germany by Paul Ramdohr (1890–1985) and his students. Essential references for ore microscopists include the text of Craig and Vaughan (1981) and the color atlases of Ixer (1990) (with an online version by Ixer and Duller (1998)) and Pracejus (2008).

The ore microscope is similar to the metallographic microscope, but has a rotating stage, is equipped with polarizer and analyzer, and requires a more powerful light source (at least 100 W). Minerals are identified by crystal form, twinning, color, reflectance, reflection pleochroism (change of color with rotation in reflected plane-polarized light, PPL), bireflectance (change of color or brightness with rotation in reflected cross-polarized light), internal reflections, and hardness (Craig and Vaughan 1981). Variations in color, pleochroism, and bireflectance, as well as internal reflections, are enhanced if oil-immersion objectives are used instead of the dry (air) objectives on metallographic microscopes. Since perception of the color

² For the use of heavy isotopes to infer the provenance of ores, slags, and metals, see the chapter by Ernst Pernicka in this volume.

and reflectance of a given mineral by the eye is conditioned by those of the minerals surrounding it, professional ore microscopists measure reflectance and color with spectrophotometers and light sources that produce monochromatic light at several wavelengths. The microhardness of grains (on the Vickers scale) is measured with a diamond micro-indenter identical to that used in metallography. Quantitative values for reflectance and microhardness for ore minerals are listed in standard reference works, such as the indispensable volume by Uytendogaardt and Burke (1985). These are very expensive accessories, however, and if they are not available, the analyst can train his or her eyes for reflectance and color with reference samples and with the color atlases of Ixer (1990) and Pracejus (2008). The relative hardness of minerals in a given section can be judged from variation in the width of polishing scratches as they pass from one mineral into another.

Uytendogaardt and Burke (1985) list optical and hardness data for more than 500 ore minerals and Pracejus (2008) provides color microphotographs of some 450. At least 30 of these are likely to be encountered by the archaeometallurgist in ore samples, inclusions of incompletely reacted ore in slags, as crystals formed from molten slags, or as minerals produced by the corrosion of metals (Table 2.2). Some occur in more than one of these contexts, while magnetite (Fe_3O_4) and cuprite (Cu_2O) are seen in all four. Ore microscopy is usually done in reflected light on polished blocks, but not all ore minerals are opaque—for example, the copper carbonates, sphalerite (ZnS), and cassiterite (SnO_2) are not; nor are most gangue minerals. It is therefore preferable in some situations to prepare samples as polished thin sections that can be examined in both reflected and transmitted polarized light (Ixer 1990). The advantages of this can be appreciated by comparing Figs. 2.2a, b.

The ore microscopist not only identifies all of the minerals present in each sample but also documents the textures of the ores. This information is used to infer *paragenesis*—the mineral association in particular locations—and *paragenetic sequence*—the sequence of deposition of the minerals through time within an ore deposit. From examination of suites of samples across ore deposits, the ore microscopist tracks the evolution of the ore-forming fluids and can infer whether the deposit was formed by a single pulse of fluids or whether there has been partial replacement of the original assemblage by later fluids. Evidence of two or more distinct periods of mineralization within a single ore deposit would have obvious implications for provenance studies by lead isotopes (Ixer 1999; Pernicka, this volume). Archaeometallurgists can use the published studies of ore deposits to infer the possible provenance of ore samples from archaeological sites, even if the ore deposits have since been mined away.

Chemical Analysis

Many ore minerals look alike in reflected light even to the trained eye, so microchemical analysis is an essential complement to optical examination in the identification of ore minerals. Conversely, distinct minerals may have identical

Table 2.2 Common ore minerals of relevance to archaeometallurgists

Mineral name	Chemical formula	Most common occurrences
Native gold	Au	Hydrothermal veins, placers
Native copper	Cu	Supergene oxidised
Cuprite	CuO	Supergene oxidised
Malachite	Cu ₂ CO ₃ (OH) ₂	Supergene oxidised
Azurite	Cu ₃ (CO ₃) ₂ (OH) ₂	Supergene oxidised
Cerussite	PbCO ₃	Supergene oxidised
Smithsonite	ZnCO ₃	Supergene oxidised
Siderite	FeCO ₃	Hydrothermal veins, sedimentary ores, BIF
Chrysocolla	(Cu,Al) ₂ H ₂ Si ₂ O ₅ (OH) ₄ nH ₂ O	Supergene oxidised
Olivenite	Cu ₂ AsO ₄ (OH)	Supergene oxidised
Clinoclase	Cu ₃ AsO ₄ (OH) ₃	Supergene oxidised
Scorodite	FeAsO ₄ .2H ₂ O	Supergene oxidised
Annabergite	Ni ₃ (AsO ₄) ₂ .8H ₂ O	Supergene oxidised
Haematite	Fe ₂ O ₃	Supergene oxidised, skarns, BIF, hydrothermal veins, laterites
Goethite	FeO(OH)	Supergene oxidised, bog ores, laterites
Lepidocrocite	FeO(OH)	Supergene oxidised, bog ores, laterites
Magnetite	Fe ₃ O ₄	Ultrabasic magmatic, VMS, BIF, skarns, placers
Ilmenite	FeTiO ₃	Ultrabasic magmatic, placers
Cassiterite	SnO ₂	Granitic hydrothermal veins, pegmatites, skarns, placers
Covellite	CuS	Supergene enriched, hydrothermal alteration
Chalcocite	Cu ₂ S	Supergene enriched, sedimentary syngenetic or epigenetic
Digenite	Cu ₉ S ₅	Supergene enriched
Chalcopyrite	CuFeS ₂	Hypogene porphyry, VMS, hydrothermal veins, sedimentary sulphides
Bornite	Cu ₅ FeS ₄	Hypogene porphyry, VMS, sedimentary
Tetrahedrite	(Cu,Ag) ₁₂ Sb ₄ S ₁₃	Hypogene porphyry, skarns, VMS, SEDEX
Tennantite	(Cu,Ag) ₁₂ As ₄ S ₁₃	Hypogene porphyry, granitic vein deposits VMS, SEDEX
Pyrite	FeS ₂	Hypogene sulphides, VMS, SEDEX, hydrothermal veins
Pyrrhotite	FeS	Hypogene sulphide
Arsenopyrite	FeAsS	Hypogene sulphide, hydrothermal veins
Pentlandite	(Fe, Ni) ₉ S ₈	Ultrabasic magmatic
Niccolite	NiAs	Hydrothermal alteration of ultrabasic rocks
Galena	PbS	Magmatic sulphides, VMS, SEDEX, hydrothermal veins, epigenetic sedimentary
Sphalerite	ZnS	Magmatic sulphides, VMS, SEDEX, hydrothermal veins, epigenetic sedimentary
Stibnite	Sb ₂ S ₃	Skarns, granitic hydrothermal veins, sedimentary epigenetic
Acanthite	Ag ₂ S	Supergene enriched, hydrothermal veins
Stannite	Cu ₂ FeSnS ₄	Granitic hydrothermal veins

chemical compositions—for example, hematite α -Fe₂O₃ (hexagonal) and maghemite γ -Fe₂O₃ (cubic). Optical microscopy, electron microscopy, and chemical analyses are therefore complementary, and any thorough investigation of ore samples will use all of these.

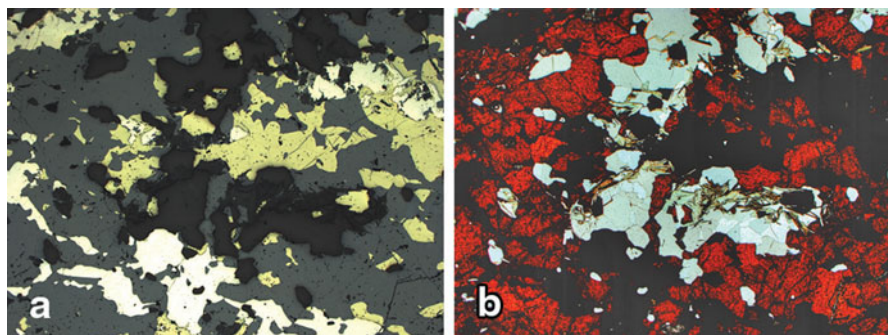


Fig. 2.2 **a** A copper–zinc ore from the Murchison Range, South Africa in reflected PPL. The width of the field is 6 mm. The two minerals identifiable in reflected plane polarized light are pyrite, FeS_2 (white) and chalcopyrite, CuFeS_2 (yellow). (Photograph by author). **b** The same field of view in transmitted PPL. This allows identification of a third ore mineral, sphalerite, ZnS (orange) and the gangue mineral quartz (gray to white) and mica (small gray and brown needles). (Photograph by author)

The standard methods for chemical analysis of individual crystals of ore minerals are energy-dispersive X-ray analysis (EDX), usually as an attachment to a scanning electron microscope, and wavelength-dispersive X-ray analysis (WDX) by electron microprobe. The lower spectral resolution of EDX can pose problems in the examination of sulphide minerals because it is unable to distinguish major X-ray peaks for lead, arsenic, and sulfur. The precision of EDX systems may also be inadequate for identifying opaque minerals that are easily distinguished by optical microscopy—for example, the common copper sulphides, digenite (Cu_9S_5 , cubic) and djurleite ($\text{Cu}_{31}\text{S}_{16}$, monoclinic). WDX systems have much better spectral resolution and are preferred for quantitative analysis.

A useful alternative to EDX is μ -XRF, which focuses X-rays to a spot 10–30 microns in diameter. Samples for μ -XRF do not need to be coated to make them electrically conductive (as is required for chemical analysis with electron beams), and with the use of appropriate filters on the incoming X-ray beam, μ -XRF can achieve lower detection limits than WDX. μ -XRF units should not be confused with portable X-ray fluorescence units (p-XRF). The latter have less powerful X-ray generators, lower spectral resolution, and more limited software than μ -XRF units, and are restricted to the analysis of relatively large areas, typically rectangles about 5–10 mm on a side. p-XRF units are very useful in the field for rapid qualitative analysis, but are less suitable for quantitative analysis than WDX and μ -XRF.

Bulk chemical analyses of ore samples from archaeological sites are generally of limited value, whether for reconstruction of technology or for inferring provenance. It is often impossible to know whether scattered pieces of ore around smelting furnaces are representative of those charged to the furnace, or whether these were pieces discarded by the smelters as unusable after further sorting of material brought back from the mines. Non-ferrous ore lumps on archaeological sites are generally of more variable metal content than are lumps of ferrous ores, because veins and gossans are

usually less homogeneous than chemical sediments, to which the great majority of iron ores belong. An exception must be made for gold and silver ores, where bulk chemical analyses or fire assays of larger samples are more meaningful indicators of precious metal content than are point analyses of individual mineral grains (though see Ixer (1999) on the implications of single-grain analyses for gold provenancing studies).

X-ray Diffraction and Raman Microscopy

Powder X-ray diffraction (XRD) is the default method of identifying minerals in an ore sample. Crushing the sample to powder ensures (except in the case of platy crystals like micas) a random alignment of crystal lattices, which ensures that all peaks for a given mineral will be present in the spectrum. This makes identification of crystalline compounds more certain than where only some of the peaks are represented, as they are with single crystals. XRD is however less sensitive than ore microscopy for detection of minerals present only in small proportion (typically less than 5 % wt) in the sample. These minor minerals may be important for inferring the geological provenance of the ore sample. Powder diffraction also requires a few grams of powder, which may be too much for small archaeological samples, and it cannot identify minerals that are poorly crystallized (cryptocrystalline), as some common minerals in the oxidized zone of copper ore deposits—such as iron hydroxides and chrysocolla (Table 2.2)—tend to be.

A powerful, swift alternative to powder XRD is Raman microscopy (Smith and Clark 2004). This is non-destructive, except for compounds (like some silver minerals) that are degraded by exposure to laser beams. It can be used on polished blocks and thin sections of ores, or even on unprepared specimens. Raman and infrared spectroscopies measure the same phenomenon, which is the momentary absorption and loss of vibrational energy by molecular bonds. Raman spectroscopy is generally the better technique for identification of inorganic molecules, and infrared spectroscopy for organic molecules, but many minerals can be identified by either method. Since Raman and infrared peaks correspond to molecular bonds, not crystal plane spacings as in XRD, both work well in identifying cryptocrystalline minerals.

While it takes about 4 h to obtain a publication-quality spectrum using powder XRD, a spectrum of comparable quality can be obtained by Raman spectroscopy in as little as 5 min, and a spectrum sufficient for identification in as little as 30 s. It is therefore an excellent technique for rapid screening of samples. When using a high-power objective (50 ×) on a polished surface, the spatial resolution is 1–2 microns, making Raman a perfect complement to optical ore microscopy. I have found it particularly helpful in studying copper ores from oxidized zones, where it is often not possible to distinguish by optical petrography between copper carbonates and copper arsenates, both of which typically form masses of very fine green needle-shaped crystals. Raman microscopy can easily distinguish between them. Raman spectrometers can even be added to some scanning electron microscopes—a shutter allows the user to switch between the electron beam and the laser beam.

The major limitations of Raman spectroscopy for mineral identification are:

- (1) Some crystals with face-centered cubic (fcc) crystal structure are not Raman active (i.e., do not produce Raman peaks). These include metallic Al, Ni, Cu, Rh, Pd, Ag, Ir, Pt, Au, and Pb, and the mineral galena (PbS).
- (2) Fluorescence can sometimes overwhelm the Raman peaks. For this reason, most Raman systems are equipped with at least two lasers of different wavelengths (typically 514 and 782 nm). The longer wavelengths are less susceptible to fluorescence, but produce smaller peaks.
- (3) Raman spectra vary with the orientation of the lattice in the crystal under investigation, and with ionic substitutions. It is essential to bear this in mind when attempting to match unknowns to reference spectra.

A particularly useful database of reference spectra for archaeometallurgists is the RRUF website (<http://rruff.info/>). This provides free downloadable XRD, infrared and Raman spectra, and chemical compositions (by microprobe) for multiple reference specimens of each of more than a thousand minerals. It includes all minerals in Table 2.2, and is continually updated with the ultimate intention of incorporating all 3800 known minerals (Bob Downs, personal communication). The site also provides free software for automatic refining and matching of XRD and Raman spectra to reference samples in the database.

Smelting Ores to Metals

Aspects of preindustrial smelting technology are spread over three chapters in this book. Discussion of the hardware required for smelting—furnaces, crucibles, tuyeres, etc.—can be found in the chapter on technical ceramics (Rehren and Martinon-Torres, this volume). The study of slags (Hauptmann, this volume) informs us on the knowledge and degree of expertise of prehistoric smelters, as inferred from the fluxes (if any) used and the temperatures and furnace atmospheres achieved. In this section I focus on the thermodynamics and kinetics of the chemical reactions that convert ore minerals to metals, and relate these to the geological considerations that I introduced above.

(a) Native metals and oxides Gold is almost always found at the earth's surface as a native metal. The PGEs (rhodium, palladium, osmium, iridium, and platinum), copper, mercury, and silver sometimes occur as native metals, but iron is very rarely encountered as the metal at the earth's surface. It usually occurs as extraterrestrial iron–nickel meteorites, which contain 5–35 wt% Ni (Buchwald 1975; Knox 1987). In a very few locations, it occurs as “telluric iron”—i.e., iron–nickel or nickel–iron pellets (often containing carbon, making natural steels and cast irons) that usually result from the intrusion of ultrabasic or basaltic magmas into carbonaceous sediments. Pellets with Ni > Fe are reported from Oregon (USA) and New Zealand, and those with Fe > Ni from Russia, Germany, and Greenland. The only known use of telluric iron was in the Arctic, where small pellets from Disko Island, Greenland,

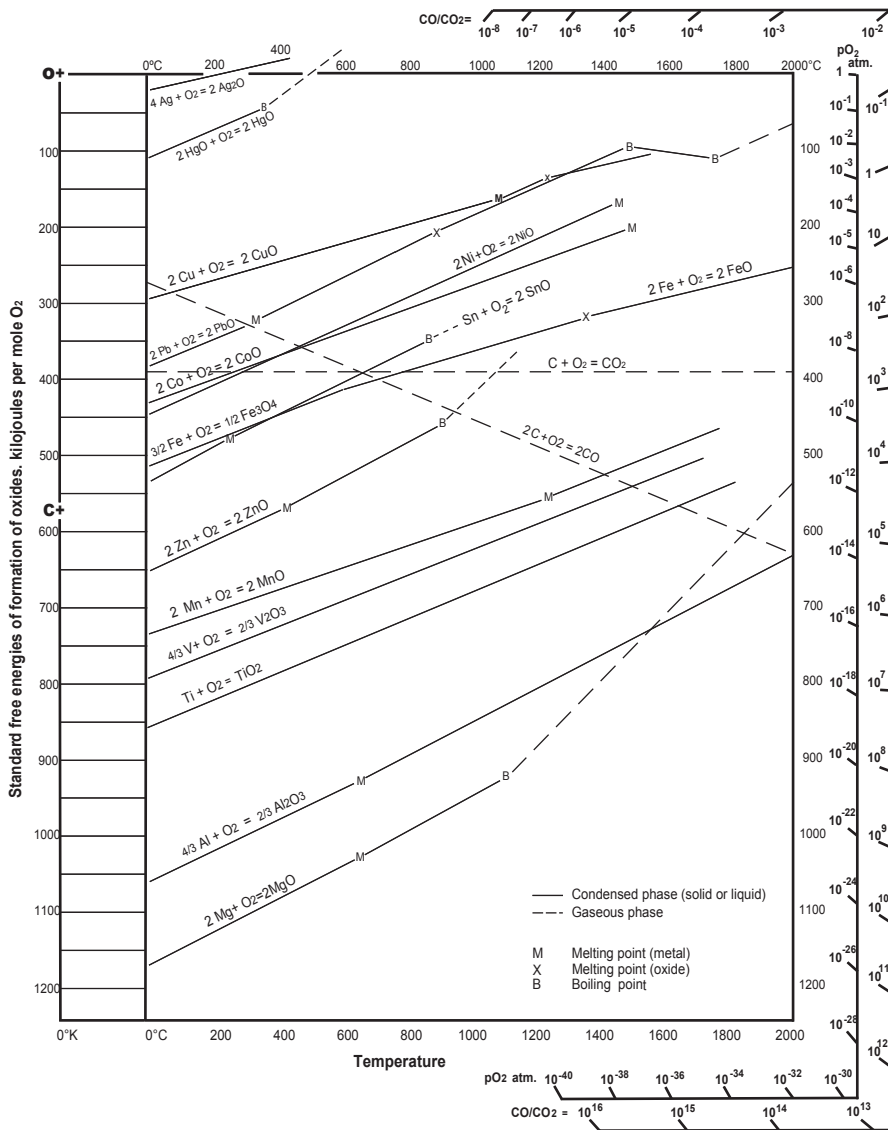


Fig. 2.3 The Ellingham diagram for the oxides of selected metals and carbon

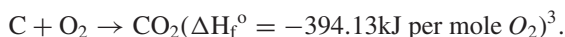
containing up to 4% Ni were cold-hammered by the Inuit for insertion into bone handles (Buchwald 1992). The other metals employed before the early Industrial Revolution (lead, zinc, and tin) are very rarely found as native metals.

These facts are well explained by the affinity of each metal for oxygen. Figure 2.3 is a plot of the Gibbs free energy of formation (ΔG) for the oxides of selected metals and carbon (y-axis) against temperature (x-axis) at 1 atmosphere pressure. This is

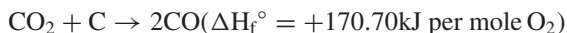
known as an Ellingham diagram and is a tool of fundamental importance in the iron and steel industry. Below each line the metal is stable; above it the oxide is stable. Since ΔG is negative for all points on this plot, the reaction of each of these metals with oxygen is exothermic (releases energy). The more negative the free energy of formation, the stronger the chemical bond formed between the metal and oxygen. Gold is not on this diagram because gold oxide has positive ΔG in the range of temperatures plotted, and thus decomposes spontaneously. The oxides of the five PGEs are not plotted either for the same reason.

The reduction of oxide to metal is endothermic (absorbs energy) in all cases, and so the lines for ΔG versus temperature have positive slopes—each oxide becomes steadily less stable as the temperature is increased. Thus, a supply of heat is absolutely necessary for smelting metals from oxide ores. However, heat alone is not sufficient; the diagram shows that only Ag and Hg oxides will spontaneously decompose to the metal at temperatures below 2,000 °C. A reducing agent that has greater affinity for oxygen than the metal is therefore also required, and for rapid reduction, the reducing agent needs to be a gas. Hydrogen is the best choice, but preindustrial metalworkers had no way to produce it. Carbon monoxide (CO) is a good reducing agent and can be produced by the controlled reaction of air with pure carbon (charcoal or coke).

Carbon monoxide is the product of two sequential reactions. The first is an exothermic reaction producing carbon dioxide:



The second step, known as the Boudouard reaction, is however endothermic:



ΔG for both reactions is plotted as a function of temperature on the Ellingham Diagram (Fig. 2.3). While ΔG for the first reaction is a horizontal line, that for the Boudouard reaction has negative slope. The two lines cross at about 700 °C. Above this temperature, therefore, CO is more stable than CO_2 , which will tend to react with charcoal to produce more CO.

The ratio of CO to CO_2 needed to reduce any metal from its oxide at any temperature in the range plotted can be found by laying a ruler across the plot from the point labeled C+ on the y-axis to the intersection of the line for the relevant metal oxide at any selected temperature. Follow the ruler beyond the right side of the plot to its intersection with the scale labeled CO/ CO_2 . The value at the intersection with this scale is the minimum CO/ CO_2 ratio required to reduce that oxide to metal at the given temperature. For CuO at 1,200 °C, for example, only 1 part CO to 10³ parts CO_2 is required. For FeO at 1,200 °C, the required ratio is about 5 parts CO to 1 part CO_2 . For Al_2O_3 at 1,200 °C, the ratio needed is about 10⁹ parts CO to 1 part CO_2 —a ratio that is impossible to achieve even in modern industry. Aluminum metal cannot be made by smelting aluminum oxide with charcoal; it is produced instead

³ ΔH_f° is the heat of formation (enthalpy) of a compound at a fixed temperature (273 K). It is related to ΔG by the equation $\Delta G = \Delta H + T \Delta S$, where ΔH is the enthalpy at a given absolute temperature T , and ΔS is entropy.

by electrolysis of molten aluminum oxide in a suitable flux, and thus the aluminum industry consumes vast amounts of electric power.⁴

We can now see that the Ellingham diagram solves the paradox that was noted above in the section on the geochemical abundance of the metals in the earth's crust. Why were the first metals used (Au, Pb, and Cu) among the geochemically scarce elements, while six of the seven most abundant metals (Al, Mg, Ti, Mn, V, and Cr) were not used until the nineteenth or twentieth centuries? The Ellingham diagram shows us that the historical sequence for the use of metals roughly corresponds to the relative affinity of each metal for oxygen. Gold oxide is unstable. Silver and copper are so weakly bound to oxygen that the oxides can be reduced to the metal by geological process, producing native metals. However, even when present as oxides, they are very easily reduced by the most rudimentary smelting technology—a shallow crucible filled with ore and charcoal, and blown with bellows or even a blowpipe powered by human lungs (Rehder 2000).⁵ Lead oxide is much more stable than copper oxide at low temperatures, and thus lead very rarely occurs as a native metal. However, above 1,000 °C the ΔG s of PbO and Cu₂O are almost identical, so the two oxides are equally easy to reduce. This is why copper and lead were the two earliest metals to have been smelted. Mercury is easier to reduce than either but is a much rarer element, and thus appears later in prehistory.

Iron is bound more tightly to oxygen in FeO than are lead and copper in PbO or Cu₂O, and thus the reduction of FeO to Fe requires a much higher ratio of CO to CO₂. Developing the technology to consistently obtain the required ratio took a very long time. Copper and lead were smelted by 5000–4600 BC in both the Balkans (Radivojević et al. 2010; Kienlin, this volume) and copper by 5000–4500 BC in Iran (Frame 2009; Thornton, this volume), but close control of the composition of the reducing gas is simply not possible in the shallow dish crucibles, blown from above, that were used in the Near East. On the Iranian plateau, crucibles were preferred to furnaces until ca. 3000–2500 BC (Frame 2009).

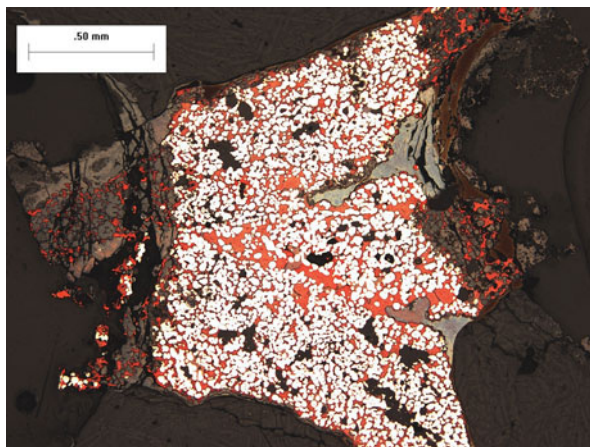
Shallow-pit furnaces appeared in the Levant around 3800 BC (Thornton et al. 2010; Golden, this volume). Even small pit furnaces powered by blowpipes can attain sufficiently reducing conditions to reduce iron (Fig. 2.4), but there is no way to separate the iron from the copper in such a furnace. The iron is simply a contaminant that must be removed by refining, which is easily achieved by remelting the raw copper in an open crucible. Since iron has a greater affinity for oxygen than copper does (Fig. 2.3), it will reoxidize, and the molten iron oxide floating on the copper can be scraped or poured off.

Shaft furnaces with upright well-plastered airtight shafts, powered by bellows connected to tuyères projecting through the walls, were developed for greater productivity in copper smelting, but they also made possible the formation of pieces of iron bloom. This is because of the large difference in the melting points of copper

⁴ Even though aluminum is the most abundant metal (Table 2.1), recycling makes good economic sense because much less energy is needed to remelt aluminum than to smelt an equivalent amount from alumina.

⁵ Many archaeometallurgists greatly overestimate the difficulty of smelting copper from oxides.

Fig. 2.4 A grain of a weathered copper–iron mineral (presumably originally a copper–iron sulphide), reduced to copper and iron metal, from a small lung-powered copper smelting pit furnace of the early second millennium CE on the Pampa de Chapparui, Lambayeque Province, Peru. (Photograph by author)



(1084 °C) and iron (1538 °C). In a shaft furnace, molten copper can drain to the base of the furnace, leaving tiny grains of hot solid iron suspended among charcoal. As these come into contact with each other, whether by consumption of the charcoal or being swept up in slag, the iron grain weld to each other. From time to time, therefore, copper workers may have found small lumps of metallic iron bloom in their furnaces.

About a dozen iron objects (including two daggers) are known from eastern Anatolia between 2800 and 2100 BC (EB II and EB III). Although some of these contain nickel, the concentrations are mostly too low for meteorites, and they are therefore tentatively accepted as smelted iron (Yalçın 1999; Jean 2001; Lehner and Yener this volume).⁶ By this time there were certainly shaft furnaces in use and the use of iron oxides as fluxes in copper smelting was widespread (see Hauptmann, this volume). It is therefore possible that iron was made very occasionally as an accidental byproduct of the smelting of copper during this period. Iron is mentioned in Old Assyrian documents from about 1900 BC on as a rare and very valuable material, reserved for royal ceremony. It was not until the New Hittite period (1400–1200 BC) that written records mentioned the use of iron for weapons (Souckova-Sigelová 2001), so it was probably during this period that metalworkers began to regularly achieve the high ratios of CO to CO₂ needed to smelt iron. The magnificent gold-handled iron dagger in Tutankamun's tomb dates to this period and is thought to have been a gift from a Hittite ruler (Vallogia 2001).

The chemical composition of iron-fluxed copper slags is very similar to that of iron-smelting slags (Hauptmann, this volume), so iron smelting does not require higher temperatures than copper smelting. What makes iron smelting in small furnaces so much more difficult than copper smelting is the fact that the Boudouard

⁶ Note, however, that Knox (1987) shows that nickel is leached from corroded meteoritic iron. As most of the earliest finds of iron are heavily corroded, the nickel content is not an infallible means of distinguishing between the two.

reaction ($\text{CO}_2 + \text{C} \Rightarrow 2\text{CO}$) is endothermic. To achieve the high CO/CO_2 ratio required to reduce FeO , much of the heat produced by the burning charcoal must be used to make CO . Yet the temperature of the furnace cannot be allowed to drop below 1,100–1,200 °C, or the slag will not be liquid enough to separate from the metallic iron (Hauptmann, this volume). When using small, poorly insulated furnaces the iron smelter must balance these two opposed requirements within a very narrow window (Rehder 2000).

From this perspective, it is easy to understand why so long an interval passed between the mastery of copper smelting and the mastery of iron smelting. It also explains quite well the widespread concerns of the last indigenous African iron smelters with witchcraft (Childs and Killick 1993). When one smelt succeeds, yet the next fails—even though it appears that the same materials and procedures were used—witchcraft provides a perfectly sensible explanation. This delicate heat balance also explains why iron smelting can only be conducted with charcoal or coke fuel. Wood, peat, and coal contain water that will absorb heat as it turns to steam, and that heat will be lost to the system as the steam leaves the furnace (Rehder 2000). Charcoal and coke are essentially pure carbon with a few percent ash (mostly oxides of calcium, potassium, and sodium).

The Ellingham diagram does not entirely explain the sequence of metallurgical innovation. Note that both nickel and cobalt are more easily reduced than iron and that nickel is more abundant than copper in the earth's crust, while cobalt is more abundant than lead (Table 2.1). The melting points of pure nickel (1,455 °C) and pure cobalt (1,495 °C) are close to the melting point of iron (1,538 °C), and both form alloys with carbon that have eutectics (minimum melting points) within the ranges of the larger charcoal-fuelled blast furnaces. Nickel and cobalt should also be reducible in the solid state by bloomery furnaces, as iron was before the innovation of the blast furnace. Yet there are, to my knowledge, no finds of smelted pure nickel or pure cobalt objects (or of their alloys with carbon) in antiquity; indeed, cobalt was only recognized as an element in 1735 AD, and nickel in 1751. This anomaly requires explanation, and for this we must turn to geochemistry instead of to thermodynamics.

As indicated in Table 2.1, both metals are strongly concentrated in ultrabasic rocks (dunites and peridotites), and much of the world's nickel supply now comes from laterites derived from weathering of these rocks. Nickel may be enriched in laterites to levels of a few percent and is mostly held in garnierites (nickel-bearing serpentine and talc). Most of these laterites consist of iron hydroxides, which are easily smelted. Iron–nickel alloys produced from laterites present in Sulawesi (Indonesia) form shiny (unetched) layers with 1–5 % Ni in some pattern-welded decorative blades (*keris*) from southeast Asia (Bronson 1987). We should also expect to find smelted iron–nickel alloys in those parts of Africa where laterites formed over ultrabasic rocks; the fact that these have not yet been noted is certainly a consequence of the very small number of chemical analyses of African iron that have been made to date.

Nickel can never be the major metal in laterites, but it certainly is in some sulphide ore deposits in ultramafic volcanic rocks and especially in komatiites (Guilbert and Park 1986: 362–367), where massive sulphides form puddles that have separated from the silicate lavas immediately above them. Nickel sulphide ores are also found

in layered mafic and ultramafic intrusions that solidified below the earth's surface (Ixer 1990, pp. 24, 25). Both types of ultramafic rock were mostly formed quite early in the development of the earth's crust, and large nickel deposits are therefore only found where extensive areas of Archean rocks are exposed. These areas are predominantly in Australia, Canada, and the USA, where there was no smelting before European colonization. Major nickel deposits do however occur in South Africa, Zimbabwe, and Russia, and minor ones in Europe (e.g., Ixer 1990, pp. 38, 39). The necessary technological conditions for smelting nickel oxides have existed in these regions for 1800–2600 years. So why is there no evidence for it?

The main reason for this is probably that nickel and cobalt oxides are quite soluble in water (hence the high values of these elements in marine clays—see Table 2.1) and thus are almost never found in gossans. Thus, the fact that nickel and cobalt oxides are relatively easy to reduce is irrelevant—there were no oxide or carbonate ores of these elements available. Nickel and cobalt ore minerals are mostly sulphides and arsenides, which look very much like copper sulphides but are more difficult to reduce. This is known to have been a source of much frustration to medieval German copper smelters, who called the nickel ore mineral now known as niccolite (NiAs) “Kupfernickel” (“devil's copper”). Western metallurgists did not realize that these ores could be roasted to oxides, and then smelted to metal under conditions like those used for iron, until the middle of the eighteenth century.

Cassiterite (SnO_2) has very similar ΔG to FeO across the range of temperatures in the Ellingham diagram. Yet the first low-tin bronzes (with up to 3 % Sn) date to ca. 3000 BC—long before iron was smelted (Thornton 2007; Frame 2009). Some archaeometallurgists (e.g., Roberts et al. 2009) have suggested that the earliest bronzes resulted from the unintentional smelting of stannite ($\text{Cu}_2\text{FeSnS}_4$) or its oxidic weathering products, but there is no direct evidence for this. Stannite is rarely a major mineral in ore deposits; it occurs instead as a minor component in hydrothermal vein and VMS deposits (Taylor 1979; Ixer 1990). It is difficult to see how stannite could be concentrated enough to feed a furnace that could produce bronze with enough tin to be visibly or mechanically different from copper.

A more probable thesis is that the earliest bronzes with more than 5 % Sn were made with placer cassiterite, but that metallic tin was not involved. Bronze can be made instead by heating cassiterite in a crucible with copper metal under a thick cover of powdered charcoal. Objects of metallic tin are very rare indeed before the Late Bronze Age in Mesopotamia and the Aegean; the oldest known are in the Royal Cemetery at Ur (Early Dynastic III, ca. 2600 BC (Moorey 1999)) and a tin–iron bracelet from Thermi in the Aegean of about the same date (Begemann et al 1992). Tin metal can be smelted from cassiterite in small batches in sealed crucibles (to minimize loss of tin oxide as vapor) with the batches later remelted to form larger ingots. (The melting point of metallic tin is only 232 °C.) This procedure will obviously not work for iron, which has a melting point of 1,538 °C. We thereby arrive at a plausible explanation for the production of tin metal so much earlier than iron, but there is as yet no direct evidence for this scenario. In summary, tin remains the mystery metal in the archaeometallurgy of the Old World—we do not know how

bronze was discovered, how metallic tin was first made, nor have we established the source(s) of the tin ores used in western Eurasia during the Bronze Age.

The early history of zinc and brass is better understood (Craddock 1998; see also the group of seven chapters in La Niece et al. (2007)). Zinc is geochemically much more abundant than tin (Table 2.1), yet brass appears later in the archaeological record than bronze. Setting aside the disputed claims for brass in the fourth and third millennia BC in China, the earliest known brass objects are at Thermi (Aegean) and date to the early third millennium BC. Thornton (2007, Table 2.1) lists 37 brass or gunmetal (copper + zinc + tin) objects dated before 1350 BC from the Aegean, Mesopotamia, Central Asia, Iran, and the Persian Gulf. However, brass did not become a common alloy in the Near East or the Aegean until the first century BC in the Roman Empire, though it was probably widespread much earlier in India. Metallic zinc appears very much later in the historical and archaeological record than brass. There are written references to it in Indian texts from the late first millennium BC (Craddock 1998) and the production of zinc appears to have been confined to South Asia until the Islamic era. It spread to, or was independently invented in China in the sixteenth century AD, but was not produced in western Europe until the eighteenth century.

These facts accord well with expectations derived from the Ellingham diagram (Fig. 2.4). Although zinc is frequently associated (as zinc carbonate) with lead and copper in oxidized ores, note that Zn has a much stronger bond to oxygen (more negative ΔG) than either Cu or Pb. With the typical CO/CO₂ ratios prevailing in early copper smelting, whether in crucibles or pit furnaces, ZnO will simply not be reduced. With the more reducing shaft furnaces, ZnO can potentially be reduced, though at CO/CO₂ ratios somewhat greater than those for FeO or SnO₂. However, metallic zinc boils above 907 °C to produce zinc vapor, which will be lost to the furnace and instantly reoxidized in contact with air. The several dozen brass objects known from early times must therefore represent very unusual circumstances where highly reducing atmospheres coincided with some means of preventing the escape of metallic zinc vapor. The only really plausible technology that satisfies both of these conditions is to heat metallic copper, zinc oxide, and powdered charcoal in a tightly sealed crucible. This was what the Romans did, and the remains of the very small lidded brass-making crucibles are among the most characteristic artifacts of Roman metallurgy (see Martinon-Torres and Rehren, this volume). The sporadic occurrence of brass in earlier millennia probably represents multiple earlier inventions of this technology that, for reasons unknown, did not become more generally adopted until the middle of the Roman era. The first production of metallic zinc, in India, required the invention of an ingenious piece of apparatus that combined an inverted crucible, packed with zinc oxide and charcoal, with a long tube to cool and condense the zinc vapor to liquid zinc. This is a form of distillation. It is not surprising that this innovation should have taken place in India, for Ayurvedic medicine had a long prior history of distillation to produce essential oils from plants (Craddock 1998).

Any oxide that is not reduced at the prevailing CO/CO₂ ratio will end up in the slag. This explains, for example, why prehistoric iron workers in South Africa were able to smelt magnetite/ilmenite ores containing up to 20 % TiO₂ (Miller et al. 2001),

but modern blast furnaces cannot use iron ores containing more than 2 % TiO_2 . The CO/CO_2 ratio in a furnace is a function both of its size and of the rate of air supply (Rehder 2000). The early hand-blown shaft furnaces used for smelting iron could not reduce the oxides of chromium, vanadium, or silicon but the early water-powered blast furnaces could. Higher CO/CO_2 ratios also favor the diffusion of carbon into metallic iron, and thus the production of cast iron (see Notis, this volume). Historic cast iron from water-powered blast furnaces contains up to 3.5 % silicon, though most of the silica will end up in the slag (Tylecote 1986, Tables 106 and 108).

Sulphide Minerals

An Ellingham diagram is also available for sulphides, but is not particularly useful for archaeometallurgists. This is because the conversion of sulphides to metals is much more complicated than the reduction of oxides to metals, requiring up to three separate operations. Sulphide ores are often physical mixtures of copper, iron, and copper–iron sulphides, sometimes also containing sulfosalts with arsenic and antimony (Table 2.2), as well as gangue minerals such as quartz and feldspars. Gangue can be reduced by washing away the lighter fraction, but iron sulphides cannot be separated from copper sulphides by washing because the specific gravities are too similar.

All of the major metal sulphides melt below 900°C , and in a strongly reducing atmosphere pure sulphide minerals will simply melt and trickle to the base of the furnace to form matte (globules or plates of copper or copper–iron sulphides). Mattes are easily recognized by their glossy surfaces and their high specific gravity. Extracting the copper from matte requires two further operations. It must first be roasted in air to remove the sulfur as gaseous sulfur dioxide, leaving behind a mass of mixed copper and iron oxides. The copper is then separated from the iron by smelting this mixture with added quartz at CO/CO_2 ratios too low to produce any iron. Under these conditions, the iron oxides combine with silica to produce a fayalitic slag, while the copper is reduced to metal and separates from the slag by virtue of its higher specific gravity. This three-step process is called matte smelting.

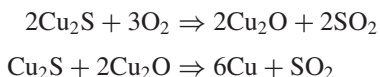
An alternative is to eliminate the separation of matte, proceeding directly to the oxidation of the ore. When the sulphides are completely oxidized (“dead-roasted”), the ore is then smelted. The iron oxides combine with gangue (augmented with more quartz if necessary) to produce slag, which separates from the copper metal. Which of these two processes is more efficient depends upon a number of factors, including the proportion of gangue in the ore and the availability of water for improvement (beneficiation) of ore grade before thermal treatments. In both cases, the copper usually needs to be refined before use.

Both of these processes are historically well documented (e.g., Agricola 1950), but it seems unlikely that they were used in the earliest stages of extractive metallurgy because of their complexity when compared to the direct reduction of oxides. For this reason, it was long believed that the exploitation of sulphide ores was a stage in the development of metallurgy that began only after long experience with the

smelting of oxide ores (e.g., Wertime 1973; Charles 1980). However, subsequent research suggests a more complicated picture. An important review article by David Bourgarit (2007) examines the mineralogy and chemistry of “slags” from 20 sites that provide some of the earliest evidence of the spread of extractive metallurgy across western Eurasia, from the fifth millennium BC (the Levant and Bulgaria) to the third millennium BC (France and Spain). Of these sites, five appear to have used oxide ores, four sulphide ores, and the remainder mixtures of oxides and sulphides. The chemistry and mineralogy of these “slags” is extremely variable. Most consist of patches of slag (i.e., assemblages of slag minerals, metals, and glass produced by crystallization of a melt) among unreacted or partly reacted ore and gangue minerals. In consequence, most do not have the mineral assemblages predicted by equilibrium phase diagrams for their chemical compositions (see Hauptmann, this volume).

These findings are prompting a major shift in thinking about the earliest smelting technologies. The remarkable scarcity of slag on the earliest copper-smelting sites in Eurasia is probably not, as previously supposed (e.g., Budd et al. 1992; Craddock 1999), a consequence of the smelting of very pure oxide ores (“slagless smelting”), but rather a consequence of the inability of many early metalworkers to effectively remove gangue as slag. The product would have had to be crushed to recover the copper, producing what Bourgarit (2007) calls “slag sands.” This realization might have emerged earlier if Old World archaeometallurgists had been more familiar with the archaeometallurgy of South America. Moche and Sican copper smelters on the north coast of Peru (mid- to late-first millennium AD) smelted small batches of ores with blowpipes, and could not fully separate slag from metal. They had to crush the product to obtain the prills, producing slag sands that form stratified deposits up to a meter deep (Epstein 1993, Fig. 17). Perhaps the archaeological methods used so far in excavating the earliest smelting sites in the Old World are not recovering slag sands in many cases?

The occurrence of sulphide minerals at many of these early sites has also attracted much interest to the argument, first made by Rostoker et al. (1989), for the production of copper metal by cosmelting sulphides with oxides. They demonstrated the feasibility of this process through laboratory experiments, and proposed the following reactions:



The first reaction can be accomplished through partial weathering of sulphides exposed at the earth’s surface, or by incomplete roasting of sulphide minerals by the smelters. The cuprous oxide then reacts with chalcocite to produce copper (cosmelting). This is an attractive suggestion because it offers a simpler *chaîne opératoire* than matte smelting or dead roasting, though it has yet to be demonstrated that it was actually employed in prehistory. Laboratory experiments under more controlled and systematically varied partial pressures of oxygen by David Bourgarit and colleagues suggest a more complicated picture when iron oxides are present as well. Iron compounds tend to remove oxygen as iron and copper–iron oxides in the slag, forcing the

sulphides to form matte in mixed sulphide–oxide furnace charges instead of reacting with oxides to form copper metal (Bourgarit 2007, Table 2.2). (But see also the discussion of cosmelting experiments below in the section on copper/arsenic/antimony alloys.)

There is clearly much that we do not yet understand about the earliest copper smelting. The way forward from here is to continue to pursue smelting experiments, such as those of Lechtman and Klein (1999) and coupled laboratory experiments, like those conducted by David Bourgarit, Benoit Mille, and colleagues (summarized in Bourgarit 2007). The methods of ore geology must play a central role in studies of the earliest metallurgy, as many of the products are essentially partially reduced ores rather than slags in the modern sense.

In light of the discussion above of the absence of evidence for metallic nickel and cobalt in western Eurasia before the eighteenth century, it must be noted that copper–nickel coins (75 mass% Cu: 25 mass% Ni) were issued by the Graeco-Bactrian kingdom (northern Afghanistan) from 170 BC. This region was in contact with China, where some copper–nickel objects are dated as early as the Warring States period (ca. 475–221 BC). Since no objects of nickel are known from either region, one can assume that these alloys were made by smelting dead-roasted copper–nickel sulphide ores under more reducing conditions than those normally required to produce copper. The melting point of a 75Cu: 25Ni alloy is just below 1,200 °C. A ternary alloy called *paktong* was later developed in China, certainly by the Ming Dynasty (1368–1644) and perhaps before. This 60:20:20 alloy of copper, nickel, and zinc melts at around 1,130 °C and was used for coins; it was imported to Europe in the seventeenth and eighteenth centuries and stimulated the development of an equivalent alloy (“German silver”). Cobalt compounds were widely known and traded within the last 3,500 years in western Eurasia, and later in the East, as colorants for deep blue glasses (Moorey 1999), but copper–cobalt alloys melt at higher temperatures than their copper–nickel equivalents. This may explain their apparent absence from the archaeological record.

Arsenical and Antimonial Copper

In both western Eurasia and in South America, we see evidence of a stage between the first appearance of smelted (nearly pure) copper and the first appearance of tin bronzes, during which copper containing a few percent of arsenic and/or antimony was used. Arsenic hardens copper as effectively as tin up to about 10 mass% As (Budd 1991). The addition of more than 3 mass% arsenic and/or antimony makes harder, sharper tools than those made of pure copper, so this innovation represents a very significant advance in the history of metallurgy. At higher concentrations (10–25 mass%), both elements make copper too brittle to forge, but they make attractive casting alloys (as seen in the late Chalcolithic hoard at Nahal Mishmar in the southern Levant—see Golden, this volume).

Ever since this stage in the history of metallurgy was recognized in the late 1950s, it has been the subject of considerable controversy. From which minerals and ore bodies did the arsenic and antimony derive? Were these alloys simply fortuitous—the result of smelting ores that happened to contain arsenic and/or antimony? Or were the arsenic and antimony concentrations controlled by adding minerals or a “master alloy” to molten copper?

Both elements are geochemically scarce (Table 2.1) and many copper deposits contain negligible amounts of either element, but in some deposits arsenic and/or antimony minerals are major components of the parageneses. The continuous series of minerals from tennantite ($\text{Cu}_{12}\text{As}_4\text{S}_{13}$) to tetrahedrite ($\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$) are known as fahlores (fahlerz), and may also be important ores of silver (which substitutes for copper). They occur mostly in epigenetic veins and were deposited from hydrothermal fluids at relatively high temperatures. Fahlores are dominant in ore deposits in some parts of the Alps, especially in Austria, and have been the subject of much speculation in archaeometallurgy as potential ores for early copper–arsenic alloys. Many of the porphyry copper deposits along the Andes also contain tennantite–tetrahedrite, or the parallel series from enargite (Cu_3AsS_4) to famatanite (Cu_3SbS_4) (Guilbert and Park 1986). Copper–arsenic alloys were widely used in Andean prehistory from ca. 800 CE to ca. 1450 CE (Lechtman and Klein 1999), but there are curiously few reports of prehistoric copper–antimony alloys from South America. Antimony is also found in quartz–stibnite (Sb_2S_3) veins, often with gold; these are most common in China. Ores with stibnite, galena, and arsenopyrite (FeAsS) often accumulate at structural traps in sediments, especially in carbonates. Arsenopyrite also tends to occur in high-temperature vein deposits around granitic intrusions, often with cassiterite (SnO_2) and tungsten minerals (Dill 2010).

Fahlores have frequently been suggested as the sources for the earliest arsenical coppers in Eurasia. (Antimonial coppers are less common.) This is unlikely for two reasons. The first is, as Ixer and Patrick (2003) note, that tennantite and tetrahedrite are hypogene sulphides (contra Craddock 1995, p. 28). Thus, they are encountered only where the supergene layer has been removed by recent glaciation, or in mountain ranges where continuous, rapid erosion prevents the formation of a supergene layer. Elsewhere they were rarely accessible to prehistoric metallurgists.

The second reason is that direct smelting of tennantite or tetrahedrite will result in the loss of much of the arsenic and antimony to the brittle intermetallic copper/iron arsenides or antimonides, which are known as speiss. Conversely, if fahlores are dead-roasted before smelting, most of the arsenic and antimony will be lost to the air as the volatile (and poisonous) oxides As_2O_3 and Sb_2O_3 , though enough can remain to allow the smelted copper to retain 2–3 % As or Sb (Höppner et al. 2005).

It has been widely assumed that during the spread of metallurgy across Europe from the Balkans (earliest metallurgy 5000–4500 BCE) to Britain (earliest metallurgy ca. 2400 BCE), early metalworkers were able to figure out fairly quickly how to smelt the various copper sulphide ores that they encountered. However, this view has recently been challenged. A few Neolithic copper slags, dating from 4500 to 4000 cal BCE (but see Kienlin this volume), have been recovered in the Innsbruck area of Austria, and analysis of them shows that smelting of fahlores was attempted.

However, lead isotopic analysis of many Neolithic copper artifacts from this region shows unequivocally that these cannot have been smelted from the fahlores, but were instead imports from eastern Europe. It was not until the Early Bronze Age (2500–2000 cal BCE) that the distinctive chemical and lead isotopic ratios of these fahlores appeared in the copper of central Europe (Höppner et al. 2005).

A popular alternative scenario for the first appearance of arsenical copper is that it reflects the direct smelting of arsenates, which occur in the supergene zone above copper–arsenic–sulfur ores (Table 2.2). This is an attractive proposition because: (1) copper, iron, and nickel arsenates are blue–green minerals that can be confused with copper carbonates and (2) they smelt directly to copper–arsenic alloys in mildly reducing atmospheres, thus avoiding the excessive losses of arsenic associated with dead roasting. The smelting of arsenates was strongly suggested as the solution to the question of the first occurrence of copper–arsenic alloys in Britain and Iran (e.g., Charles 1980; Budd et al. 1992; Pigott 1999). This is certainly a plausible option, but it is one that has the potential to entrap unwary archaeometallurgists. As the ore geologists Ixer and Patrick (2003) have warned, the fact that arsenates appear on lists of minerals from a given mine does not mean that they were ever present in quantities large enough to be potential ores for prehistoric metallurgists. Nor does their presence on spoil piles mean that they were even present in the supergene zone. Ixer (1999) notes that spoil piles (which he terms “supragossans”) are fertile environments for the growth of new minerals under very different conditions than those prevailing underground.

The same caution applies to the argument of C. S. Smith, summarized by Pigott (1999) that the earliest arsenical copper on the central Iranian plateau was made by simply dissolving the minerals domkeyite (Cu_3As) and algodonite (Cu_6As) from the Talmessi/Anarak/Meskani mining district into molten copper. At this point in time speculative arguments serve no further purpose; archaeometallurgists need to produce the proof, which can only come from very detailed studies of ores and slags from well-dated archaeological contexts. Frame (2009) shows the way forward with her identification by Raman spectroscopy of algodonite in Chalcolithic levels at Tal-i-Iblis. Lead isotope analysis of these minerals is compatible with those of Talmessi/Anarak/Meskani, some 500 km distant, in which algodonite is a documented ore mineral.

A third pathway to copper–arsenic–antimony alloys is through cosmelting of copper oxides with copper–arsenic–antimony–sulfide minerals. The viability of this pathway has been directly demonstrated by the smelting experiments of Lechtman and Klein (1999). Their work focused on understanding the production of these alloys in South America, and used actual ores from the region. Copper “oxide” minerals (actually the hydroxychloride minerals atacamite ($\text{Cu}_7\text{Cl}_4(\text{OH})_4$) and paratacamite ($\text{Cu}_2\text{Cl}(\text{OH})_3$), which are major ore minerals along the arid southern Peruvian coast) were mixed in varying ratios with enargite (Cu_3AsS_4) or arsenopyrite (FeAsS). These were smelted in uncovered crucibles (little exposure to CO), and also in a small furnace (full exposure to CO) at relatively low temperatures ($< 1,100^\circ\text{C}$) and at mixtures from 1:1 to 4:1 of the hydroxychlorides and sulfosalts. Copper–arsenic metal was produced in all cases except for the 1:1 mixtures; arsenic contents in the metal were

from 7 to 26 wt%, the higher contents occurring where arsenopyrite was used. Matte and speiss were also produced, but in most cases separated cleanly from the metal. The results obtained are not directly comparable to archaeological finds because their crucible and furnace charges generally contained too little silica to form silicate slags, but they do establish without doubt that oxide–sulphide cosmelting provides a plausible mechanism for the initial production of copper–arsenic–antimony alloys. Which of these potential *châ ines opératoires* was actually used at a given smelting site must however be established by very detailed investigation of all the material evidence—ores, mattes, speisses, slags, refractories, and metal—in each case by the appropriate specialists.

Conclusions

The main message conveyed here is that the historical development of extractive metallurgy cannot be fully appreciated without some understanding of ore geology and geochemistry. Although geological perspectives have been fully integrated into archaeometallurgy in the German-speaking areas, they have often been absent from Anglophone and Francophone archaeometallurgy. Anglophone archaeometallurgists have been particularly prone to poorly informed speculation about ores and ore sources used in the past.

The deeper we dig into the prehistory of metallurgy, the more we need teams of collaborating specialists. To investigate the prehistory of extractive metallurgy, we need teams that include (at minimum) specialists in economic geology; the archaeology of mines and metallurgical sites; the interpretation of ores, slags, refractories, and metals; experimental replication of smelting processes in field and laboratory; and in inferring the geological provenance of ores and metals by chemical and isotopic techniques.

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