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 (Higueras 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 2.8×10^6x.

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 Kupferscheifer, 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 (FeS_2) and chalcopyrite ($CuFeS_2$). 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 (Cu_2O, red), malachite ($Cu_2CO_3(OH)_2$, green), and azurite ($Cu_3(CO_3)_2(OH)_2$, 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:

$$2Cu_2S + 8Fe^{3+} + 12(SO_4)^{2-} \Rightarrow 2Cu^0 + Cu_2O + 8Fe^{2+} + 12H^+ + 14(SO_4)^{2-}$$
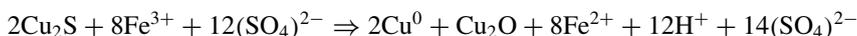
(Guilbert and Park 1986, Eq. 17.19).

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

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[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).