Iron Not Second Most Abundant Element

To the Editor:

In the June 1993 issue of the *MRS Bulletin,* K.J. Anderson presented some misinformation concerning the abundance of iron ("Forging Iron," p. 64). Iron is not the second most abundant element on earth after aluminum. For the total earth, by mass, iron is the most abundant at 34.6%, followed by oxygen at 29.5%, silicon at 15.2%, magnesium at 12.7%, calcium at 1.1% and, finally, aluminum at 1.1%. In the earth's crust, iron is fourth, behind oxygen, silicon, and aluminum.

Professor Nicholas E. Pingitore
Department of Geological Sciences
The University of Texas at El Paso

Recent Information Overlooked in "Forging Iron"

To the Editor:

I am writing in regard to the Historical Note on "Forging Iron" that you published in the June 1993 issue of the *MRS Bulletin* (p. 64). I am pleased to find that you consider the history of materials and their development a subject worthy of so much valuable editorial space in your journal, and I hope that you will continue to give attention to this subject. Ancient materials and their processing have been under intensive study in recent decades, with results that have appeared in many journals, including yours (the January 1992 issue, for example, is devoted entirely to art and technology.) Unfortunately, this more recent information has been overlooked in the Historical Note on "Forging Iron." Much of the information in it is more representative of the subject some decades ago than of our present understanding.

While it is true in general that "very little pure iron is found in rocks," telluric iron (native iron) as well as meteoritic iron were materials often used by Arctic peoples. Distinguishing these forms of iron from each other and from smelted iron obtained in trade[1] is information important to the archaeologists and anthropologists who study the Inuit people and their contacts with other peoples.

Elsewhere, the use of meteoritic iron in objects is more rare than once believed. According to Professor Tsun Ko, Director of the Center for Archaeometallurgy at the Technical University of Beijing, there are only nine confirmed cases of meteoritic iron in ancient Chinese objects. Two of these are in the collections of the Freer Gallery of Art at the Smithsonian Institution.[2] The presence of nickel in early iron is no longer taken as sufficient proof of meteoritic origin, since objects of smelted iron containing appreciable amounts of nickel have been found in prehistoric contexts.[3] That the "ancient Aztecs made implements of meteoritic iron" and "prized their meteoritic tools above gold" cannot be confirmed by reference to Buchwald's exhaustive study of all known iron meteorites,[4] although other uses of meteoritic iron by native peoples are recorded.

In "Forging Iron," the author presents a bonfire theory of smelting iron that holds that smelted iron "was probably first discovered...in ashes of fires built on outcroppings of red iron ore." How the necessary control over the access of oxygen so as to produce consistent and highly reducing conditions is not explained. There may be some confusion here with the one metal that can be smelted in something similar to a bonfire using only natural draft. That is lead. Overman described the method used to smelt galena (lead sulfide, PbS) on the American frontier, briefly, as follows: "If a Western backwoodsman wants shot or bullets, he will kindle a fire in a hollow tree or an old stump of a tree, place some galena on the charred wood and melt it down. After cooling, he finds the metal at the bottom of the hollow."[5] Among archaeometallurgists it is generally agreed that iron was first smelted as a byproduct of copper smelting, where iron was present in the ore or iron minerals were added as a flux.[6]

Though it is a matter of ordinary experience that "iron artifacts do not last a long time," the loss of ancient iron artifacts is not entirely to be blamed on the effects of corrosion. Wrought iron was recyclable. Such recycling was done by welding pieces together and reforging. We are not able to estimate the percentage of ancient iron objects that have survived to the present simply because we do not know the original production figures, nor do we know the amount of ancient iron that remains to be discovered. Among those iron artifacts that have survived, the article mentions that "small items have been found in Egypt's Great Pyramid of Giza (2900 B.C.)." This refers to the small plate of heavily mineralized nonmeteoritic iron excavated in 1837 by J.R. Hill in the Great Pyramid of Gizeh. Because its location was not in a sealed context and the pyramid has been extensively quarried in the past, the antiquity of this artifact has always been in question. Nevertheless, a recent study concluded that its composition and structure are consistent with the date of the pyramid.[7]

The monopoly in iron once thought to have been held by the Hittites (and later, as described in I Samuel 13:19–21, by the Philistines) is not supported by evidence of archaeological finds.[8] What the "recarburization" process was that the Hittites are said to have discovered presents a puzzle, since one cannot recarburize what was not carburized to begin with. At that time, iron was not smelted as cast iron in a blast furnace but was produced directly as low-carbon wrought iron. Carburization of this iron by solid-state diffusion could be discovered by an experienced blacksmith, and is likely to have been invented independently in more than one place.

That "iron was superior to bronze" is perhaps more evident to the modern metallurgist than it was to the ancients, who had wrought iron, but had no alloy steel to compare with the products of a highly developed bronze industry. For example, not until this century, when stainless steel was introduced, was bronze displaced as a corrosion-resistant alloy. As for the suitability of bronze "for weapons use," one has only to recall the elegant Greek helmets and other bronze pieces of armor. The economic comparison that iron was "less expensive than stone for agricultural implements" is not supported; neither was iron used exclusively for objects of war and agriculture. A greater number of iron artifacts from the bronze age are in the form of pins or other jewelry.

Other evidence that iron was seen first as a rare, precious, or decorative material is abundant, such as the "iron dagger found in Tutankhamen's tomb." A miniature headrest was the only other iron object found there. Not mentioned was another dagger found in the same tomb. It is made entirely of gold (including the blade) and is similar to gold daggers recovered from other Egyptian tombs.[9] Its sheath, also in gold, bears motifs that appear more western Asiatic than Egyptian. The daggers may have been made in Egypt by west Asiatic craftsmen (since such craftsmen are depicted in Egyptian tomb paintings) or by Egyptian ones but, in fact, where they were manufactured and by whom remains simply speculation. Tutankhamen's tomb and its contents date to circa 1300 B.C. It was not "around this time" but nearer to 600 B.C. that "the Chinese independently created a blast furnace."

There is confusion in terminology, "ironworking" being used to refer to iron smelting. The description of the "hard spongy-looking mass" said to be produced in smelting is that of an iron bloom. Until recently, blooms that have been recovered archaeologically, mainly from northern Europe, were considered furnace products. At present, they are considered to be the result of considerable forging to consolidate the iron smelted in the furnace. This iron is in a rather fragmented and slaggy form, and to "reheat and hammer this mass several times" is inadequate. Peter Crew has, on the basis of his replication experiments, estimated that a small bloom requires some 40 to 60 forging heats to produce the compact forms found archaeologically.[10]

If we are to judge by the presence of the smith in early mythology—the god Hephaestos among the Greeks, and Vulcan among the Romans, for example—the smith held an important place in society long before "A.D. 1000." Nevertheless, there is good evidence from remote areas of Europe at this period and for later centuries, especially from Iceland and Scandinavia, that smelting and smithing did not constitute a craft specialty. Instead each farmer was his own smith, and this may well have been true of most of Europe during the Dark Ages.

The 14th century introduction of "a larger and more efficient design for a blast furnace" has been confused with a description of the Catalan forge. A Catalan forge is a hearth without a chimney, not a blast furnace. The product of the Catalan forge was wrought iron, whereas a blast furnace produces cast iron. A direct form of smelting, the Catalan process was developed perhaps as early as the 10th century in the Pyrenees, where it survived until 1878. It did not require a large installation and was adopted in many countries, including the United States.[11]

The appearance in Europe in the 14th century of the blast furnace itself (not "a larger and more efficient design for a blast furnace") seems to have resulted, at least in part, from the harnessing of water power. Power was needed to force air through the charge of ore and charcoal in the blast furnace stack. It has been suggested that Chinese workmen, imported to ease the acute labor shortage in Europe after the Black Death, may have brought this technology with them. Certainly there are interesting parallels with eastern designs in the earliest European blast furnaces.[12]

The charcoal that was used in blast furnaces was not burned from "wood chips" but from logs. Charcoal in too fine a form, called "breeze" because it carried heat from the furnace as it was blown out the top of the stack by the blast, led to serious heat losses and was avoided. Charcoal was, for the most part, not produced "in sealed ovens" but in heaps covered with dirt located where the wood had been felled, a method still in use in many parts of the world.

It is true that in England a fuel crisis developed due to iron smelting, and "Supplies of charcoal eventually became difficult to obtain as nearly all available forest land was chopped clear." This was a critical issue for a seafaring nation that needed timber for shipbuilding. Elsewhere, shortages did not exist and the shift to coke in the 18th and 19th centuries, where it occurred, was due to other considerations. Wood was plentiful in places like Scandinavia, Russia, and the United States. The production of charcoal iron in the United States, for example, did not peak until the 1890s.[13] Charcoal iron was preferred for some applications, such as the wire needed for telegraph lines and barbed wire fencing.[14]

In most places where coke was a useful alternative to charcoal, it was because of its greater mechanical strength. Coke could support a taller burden in the blast furnace shaft than charcoal could bear. This allowed blast furnaces to be built twice as high, with greater capacities and resulting economies of scale.

That "coal had never been suitable... because of its high sulfur content" was indeed true for iron smelting, but not "for iron working." Coal is still being used as a fuel in blacksmiths' forges, where there is an easy access to oxygen. Any sulfur present combines with the oxygen before it can diffuse into the iron.

The "cementation process" was not "developed in England," though it was extensively exploited there and was the method used in making Sheffield steel. This method can be traced back to Eastern Europe and reached Western Europe ca. 1601, in Nürnberg.[15] This was by no means "the first method of making steel." There were many methods of carburization known earlier, as documented by Biringuccio.[16] The importance of the cementation method of carburizing iron lay in its capacity for the mass production of steel; that level of production was not exceeded until the problems of quality control in Bessemer and open hearth steel, particularly phosphorous removal, had been overcome in the late 19th century.

In fact, the cementation of steel remained a commercial process until only a few decades ago. Cementation furnaces in England were shut down in the 1930s because of the economic effects of the Great Depression, but were once again brought on line during the critical steel shortages of World War II. The last working cementation furnace, Daniel Doncaster and Sons No. 5, was shut down in Sheffield in 1951.[17]

The "alternative cementation method" described ("to stack layers of high-carbon iron with low-carbon iron, heat them, then hammer them together") was not intended to produce a "homogeneous mass." Quite the opposite. What is being described here is pattern welding, where layers of hard steel, that will hold an edge, are laminated with layers of softer but tougher iron, that will not break on impact. Though pattern-welded blades are sometime referred to as "damascened" blades, genuine damascus blades were made from a crucible steel from India.[18]

The British, after they entered India in the 18th century, reported observing the Indians in several districts producing ingots of molten steel that they called "wootz." The production of crucible steel, therefore, is no longer considered the invention of Benjamin Huntsman, although he is credited with the development of the special ceramic for the crucibles from local materials. In Huntsman's process, the charge had already been made into steel in the cementation furnace and was simply melted down to produce a homogeneous product. The Indian method differed in that the charge was wrought iron and charcoal, and that the iron was carburized and the resulting steel melted—both in a single operation. The ingots produced were of a very high carbon steel and had a solidification pattern that when forged out, was compared to the pattern of damask, a textile that got its name from Damascus. There is no evidence that damascus swords were ever made in Damascus.

For the history of these and later developments in steelmaking, Barraclough's three volumes[19] are highly recommended. Refereed journals such as *Historical Metallurgy*, the *Journal of the Historical Metallurgy Society*, and *Archeomaterials* are devoted to the history of materials, as are special issues of journals such as the *MRS Bulletin*. Unfortunately the Bulletin's historical note on "Forging Iron" seriously misrepresents the level of current scholarship in this field.

Martha Goodway
Conservation Analytical Laboratory
Smithsonian Institution

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Response:

I would like to thank Professor Pingitore for pointing out an error in my "Forging Iron" Historical Note (June 1993). For such basic information, I relied on a source no more detailed than the *Encyclopedia Brittanica,* and I managed to misquote. The sentence should have stated that iron is the second most abundant *metal,* rather than element. *Brittanica* makes no distinction between abundances in the crust and in the core, but I'll certainly defer to Professor Pingitore's expertise.

Martha Goodway has added many fascinating details, some of which were new to me and some of which I was unable to include in my brief treatment. (Her original letter was twice as long as the Historical Note itself.) In these monthly articles I have tried to keep a balance between narrow subjects that can be thoroughly discussed within the limitations of 1,000 words, and much larger subjects—such as forging iron—that can be described only in broad strokes. In her letter, Dr. Goodway suggests numerous other references for further reading, including recent research I did not take into account; I hope the Historical Note may have piqued the interest of some readers.

Dr. Goodway and I share a belief in the importance of the historical aspects of materials science. While researching these articles every month, too often I have found entire volumes on a subject with only a sentence or two devoted to the development of the field under discussion. Scientific discoveries do not occur in isolation, with no connection to previous work. With these recurring Historical Notes, I hope I have placed some developments in context.

K.J. Anderson

Biological Materials are the Smartest

To the Editor:

With my usual promptness, I have just read the April issue of *MRS Bulletin.* Papers in that issue strengthen yet again one of the underlying premises of the Materials Research Society—the value of bringing investigators from disparate fields together to realize the applicability of research in one field to that of another.

Of specific interest in this issue was the juxtaposition of the "Material Matters" article on biomolecular materials ("Nature Makes a Material Diffrence," by Christopher Viney) and the series of papers on "smart" materials (R.E. Newnham, guest editor). It should be noted that biological materials were the first smart materials, and remain the most sophisticated. The protein hemoglobin, for example, modifies its ability to deliver oxygen to the tissues on the basis of the acidity and CO_2 levels in its environment. (Acidity and CO_2 levels are direct indicators of the state of the tissues and their need for oxygen). The enzyme glutamine synthetase modifies its functioning in response to the amounts of eleven different molecules, one of which modifies its own functioning in response to the levels of six other molecules. As in the case of hemoglobin, the lack of each of the seventeen effector molecules is an indicator of the state of the cell and its need for a functioning glutamine synthetase.

Mark Alper
Associate Division Head
Adjunct Professor, Biochemistry & Molecular Biology
University of California at Berkeley

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harperj@watson.ibm.com

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(505) 845-8629 • Fax (505) 844-2974
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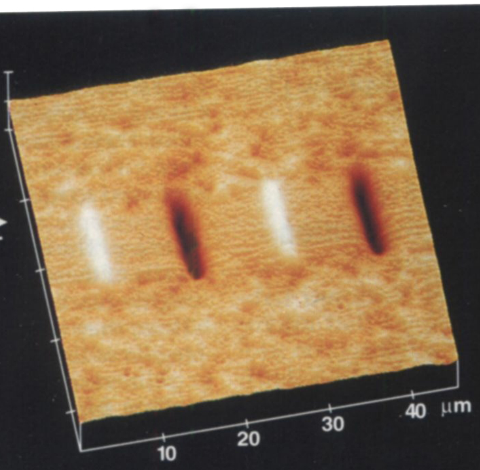
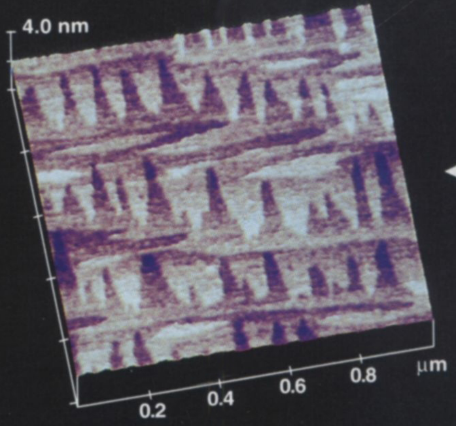


Magnetic Force Gradients ▶

These hard disk bits were written with alternating polarity and a slight skew. The speckle above and below the recorded track is due to the disordered magnetic domains in the virgin media.



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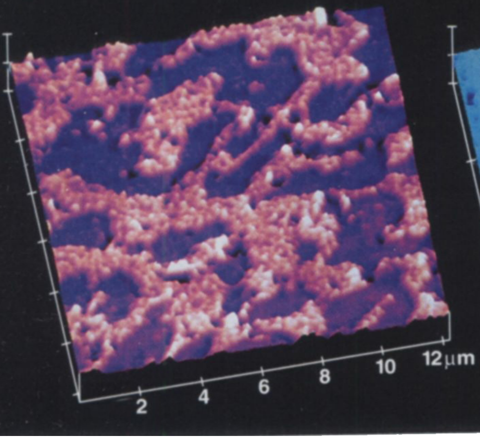

Lateral Force (Friction) ▶

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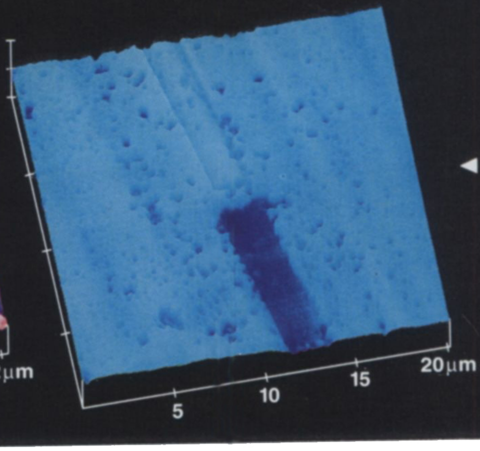

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