PERSPECTIVES: PALEOENVIRONMENTAL RESEARCH

Tales Told in Lead

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Every metal marks a romantic chapter in human history. Although there was no Lead Age to rival the Copper, Bronze, and Iron ages, lead nevertheless has appeared in all phases of art, medicine, and technology and can claim first place among metals in tonnage produced or released to the environment. It was the first metal to be extracted from its ore, and with this discovery, humankind awakened to metal technology. Because of the widespread commercial applications of lead, the records of its mining and use have opened a window on past cultures, customs, trade routes, and early methods of mass manufacturing (*1*). As reported on page 1635 of this issue, Shotyk *et al.* (*2*) have used the accumulation of lead in Swiss bogs to decipher past changes in worldwide lead production, and thus the global and regional changes that influence atmospheric lead transport.

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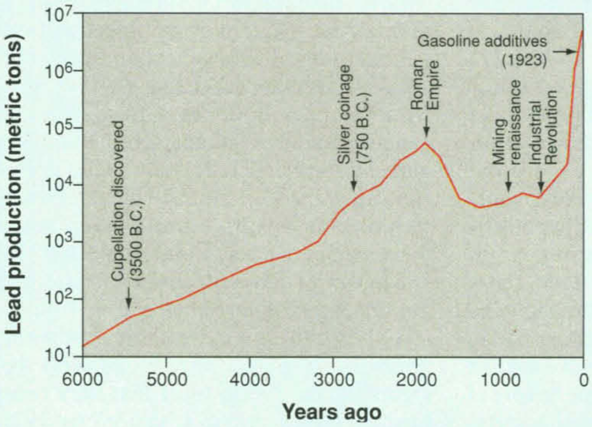
As a result of their affinity for silver, lead deposits were eagerly sought in ancient times. The Greek mines at Laurium operating well before 3000 B.C. (*3*) and the mines of the Iberian Peninsula beginning during the Iron Age are both celebrated for their contributions to the wealth of nations. Likewise, ancient Persian kings owed their legendary wealth to abundant lead/silver deposits (*4*). A breakthrough for extracting silver from lead ores, called cupellation, appeared around 3500 B.C. and greatly enhanced the popularity of silver. By the third millennium B.C., silver taken from lead ore had become the chief unit of exchange in the Near East (*5*), and the technology rapidly spread to other parts of the Old World. Cupellation remained the dominant process for silver recovery for nearly 5000 years, an important consideration in using archived lead in bogs and other deposits for paleoenvironmental detective work (*2*). By my estimate [revised from (*4*)], annual production was about 160,900, 11,000, 32,000, and 6000 metric tons during the Copper, Bronze, Iron, Roman, and Barbaric ages, respectively. Total production to 1000 A.D. is estimated at 32 million tons. Singer (*6*) estimated that about 134 million tons of lead was discovered in the Old World throughout recorded history. Thus, about 24% of the discovered lead reserves were mined in ancient times, a more reasonable figure than previous higher rates (*1*, *7*).

The introduction of silver coinage in Persia around 750 B.C. was a major stimulus for further mining. By Roman times, almost every major lead/silver deposit in the Mediterranean and Western Europe had been discovered. I estimate that annual production was much lower, about 50,000 tons per year at most (*4*). To put this in perspective, note that worldwide lead production did not reach 50,000 tons per year again until the 1820s (see figure), after the Industrial Revolution had ushered in advanced mining technologies and a huge demand for lead. Whereas the fall of Rome reduced mining in the West, many Asian mines remained productive (*8*). A revival of mining in Europe during the 11th century A.D. began in the Harz Mountains, followed by the rich silver mines of Freiburg in 1170 and the Mansfeld lode in the Rammelsberg (Silesia) in 1215. Several mines were worked in Derbyshire in the time of William the Conqueror, and the technological ascendancy of Western Europe during the Middle Ages owes much to the lead/silver mines of central Europe. In the New World lead was first mined in Virginia in 1621, and from 1700 onward, the great Mississippi Valley deposits came into prominence. Large-scale mining of lead in the famous Broken Hill district of Australia began in 1850 (*3*).



Progress in lead. Logarithmic plot of historical lead production over time. [Based on (*4*, *10*)]

Several developments influenced lead production in post-Roman times. The Saigerverfahren method (melting copper ores with lead to recover the silver), introduced between 1460 and 1480, severed the link between lead and silver supplies. The discovery of the mercury amalgam (Patio) process for nonlead silver ores of South America in 1560s supplanted cupellation as the principal source of silver (*9*). As American silver flooded the European and Asian markets, many local mines closed. Between 1000 A.D. and 1500 A.D. global lead production fluctuated between 4000 and 7000 tons per year (see figure). The low global output fits with what we know about mine production in Europe, Japan, and China (*9*). The fact that the Etang de la Gruère bog in Switzerland shows a very suppressed signal during this period (*2*) is evidence that production must have been fairly small. The steady rise in lead production from the middle of the 18th century continued for more than 200 years and peaked (at a little under 4 million tons per year) during 1979–1980 (see figure). During this time, lead was mined in many countries, and the accumulation in Swiss bogs reported by Shotyk *et al.* (*2*) nicely mirrors this spectacular increase in worldwide production and emission of lead (*10*). The all-time quantity of lead produced from mines is estimated to be about 260 million tons, and about 85% (226 million tons) of the output has occurred since 1800 A.D.

Industrial lead emission occurred in five stages that were closely intertwined with technological development. During the first, most emission came from lead/silver production. Because lead was a by-product, every effort was made to convert most of it into smoke. Stage II, from about 1450 to 1750 A.D., began with the discovery of the method for recovery of silver from polymetallic ore, which caused increased emission of lead from smelting of other base metals, especially copper. Wood was the primary fuel during stages I and II. The Industrial Revolution ushered in stage III, when fossil fuel (especially coal) combustion became an important source of industrial lead emission. The balkanization of operations and development of tall stacks during this stage greatly expanded the potential areas of impact of a given plant. Stage IV, from 1923 onward, was marked by emissions from mobile sources, especially automobile tail pipes. We are entering stage V in which the

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recovery and recycling processes for old lead are becoming a significant source of this metal to the environment.

Lead and silver mining involves three steps: (i) smelting of the lead ore, (ii) purification of the crude lead bullion, and (iii) desilverizing of the lead. At first, operations were crude and often consisted of a pot, a small pit, or simply a heap of rocks on a hillside, arranged so that natural air drafts would stoke the fire. This primitive smeltery—though cheap and versatile—released lead fumes to the air. In ancient times, about 10 to 20% of the lead mined and cupelled was released to the atmosphere (*4*). Improvements in smelting technology reduced the emission factor to 5 to 10% during stage II, and by the mid-19th century (stage III), 2 to 5% of the lead was carried away in the fumes (*11*). From the emission factor, the worldwide flux of anthropogenic lead to the atmosphere is estimated to be 5000 to 10,000 tons per year during the Roman era. Several studies have identified the Roman lead pollution in many parts of Europe, including the snow fields of Greenland (*12*). From about 500 to 1500 A.D., worldwide lead emissions fluctuated between 500 and 1500 tons per year. A steep increase in global lead emissions that began around 1750 A.D. peaked around 400,000 tons per year during 1970 to 1980 and has declined to about 100,000 tons in recent years (*10*). During the last 250 years, emissions of lead have been elevated by a combination of increased industrial demand, large-scale combustion of lead-containing coals, and automobiles. In more recent times, pollution controls have led to a dichotomy—emission rates in the developed countries are going down while those of the developing countries are still increasing (*13*).

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PERSPECTIVES: GEOPHYSICS

Oceanic Effects on Earth's Rotation Rate

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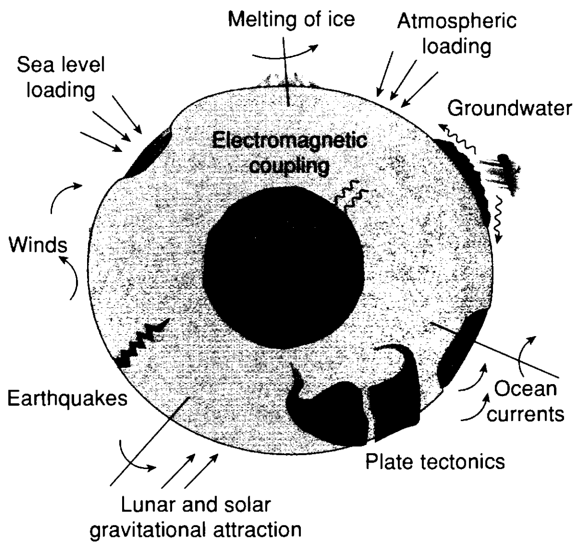
The oceans are vast in extent, fundamentally important to Earth's climate and environment, and difficult to observe. Throughout history, ship-board studies have sampled only a fraction of the ocean's volume, and observations from space, although often global, are limited to properties detectable at the surface. Thus, it is exciting when a fundamentally new observation becomes available, especially one that is global and samples the full depth of the oceans. On page 1656 of this issue, Marcus *et al.* (*1*) report on one such new measure of ocean change—variations in global ocean angular momentum. The new results reflect changes in distribution of mass, which alter the moment of inertia of the oceans on the rotating Earth, and changes in east-west currents, which alter momentum relative to Earth.

Marcus *et al.* estimate ocean angular momentum changes indirectly, using the principle that total angular momentum within the Earth system is conserved (with the exception of changes due to predictable torques applied by the sun and moon). This is the same conservation principle that allows a spinning ice skater to increase angular velocity by redistributing mass (drawing in the arms). The directly measured quantity, therefore, is Earth's rate of rotation, or the corresponding length of the day (LOD), observed in an international effort that relies mainly on the radio astronomy technique of very long baseline interferometry. This method uses radio telescope arrays to determine the speed of rotation and orientation of Earth relative to the reference frame formed by extragalactic radio sources; thus does radio astronomy become an oceanographic science.



As the world turns. Forces (arrows) acting on the solid Earth that may change its rotation. Atmospheric and oceanic forces apply torques (axes), which transfer angular momentum between the solid Earth and the atmosphere or oceans. Some of the effects illustrated, such as plate tectonics, are unlikely to contribute significantly to Earth rotation variations at seasonal to subseasonal time scales. [Adapted from (*3*)]

If total angular momentum of the Earth system is conserved, it follows that when the solid Earth loses angular momentum (and the LOD increases), another reservoir of angular momentum must have gained. It is now well known that predominantly the atmosphere is that reservoir. Numerous studies over the past two decades have shown that, to good approximation, the solid Earth and atmosphere simply trade angular momentum with one another over a variety of time scales, ranging from days to years. This is the conclusion to be drawn from figure 2A in the report by Marcus *et al.* (*1*).

There are, of course, additional reservoirs of angular momentum in the Earth system, including the oceans, polar ice sheets, and others, as illustrated in the figure. Not all of these are active on all time scales, and only those involving air and water are likely to be important at seasonal to subseasonal scales. Marcus *et al.* show that, after the atmosphere, the oceans are the next most active reservoir, at seasonal and shorter time scales. The demonstration is accomplished by forming

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