

Mystery of Timna's iron solved by lead isotope 'fingerprinting'

Scientists have long sought a means to discover where precisely the ancients obtained the ores from which they extracted their metal. Noël Gale and Zofia Stos-Gale describe a "fingerprinting" process by lead isotopes in which they are concerned at the Department of Geology at Oxford University, and which has been applied to solve the mystery of the occurrence of iron at Timna long before its common use.

A solution of the problem of indentifying the source of ancient ores is of great importance to archaeology since it would establish beyond doubt trade routes in the metals, cultural contacts and the technology and economy of ancient societies.

Attempts to solve the problem by chemical analysis of metal artefacts and ores have foundered, and metallurgical investigations have fared little better. As Professor Coles of Cambridge recently observed: "Chemical analysis of the metal products of the European Bronze Age is perhaps the most monumental disaster of all the contemporary studies . . . it has provided a few answers in restricted areas of enquiry and created mass confusion in others."

The failure of this approach is partly due to the heterogeneous distribution in most ore deposits of the minor elements on which reliance has been placed. Moreover, as Professor Tylecote's experiments have shown, the process of extractive smelting disrupts the pattern of major, minor and trace elements existing in the original ore.

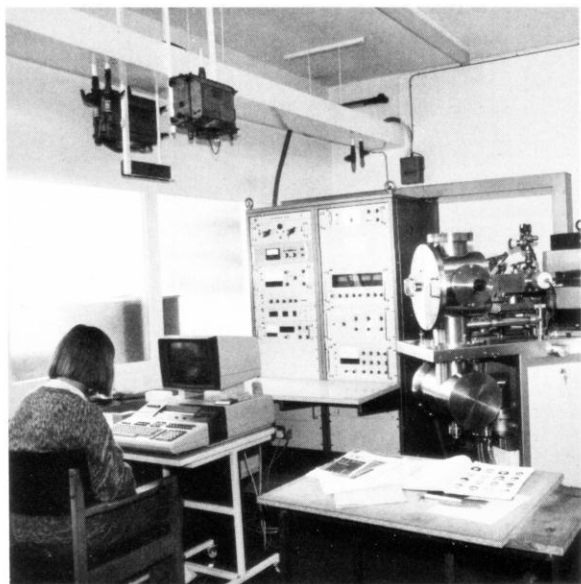
Fortunately, an alternative scientific approach to this problem exists: lead isotope analysis.

Most elements are composed of atoms of different mass. These are called isotopes. For instance, lead consists of the four isotopes Pb-204, Pb-206, Pb-207, and Pb-208, having masses respectively of 204, 206, 207 and 208 atomic mass units. The chemical processes of smelting, refining and even corrosion leave the original proportions of the lead isotope composition unchanged from that in the original metal ore.

. . . marks the spot

The isotopic composition of the lead in an ancient metal object therefore provides a "fingerprint" which allows the ore source to be pinpointed. All that is necessary is to compare the isotopic composition of the lead in the artefact with those of ores from various

Lead boat model dating to the 3rd millennium BC from the island of Naxos in the Aegean



Mass spectrometer used for lead isotope analysis at Oxford: Zofia Stos-Gale at the controls

ancient mines. Not only can this be applied to lead objects, but also to those made of silver and to copper-based alloys which always contain traces of lead derived from lead impurities in the ores.

Modern mass spectrometers make it possible to measure the lead isotope composition using as little as one millionth of a gram of lead metal.

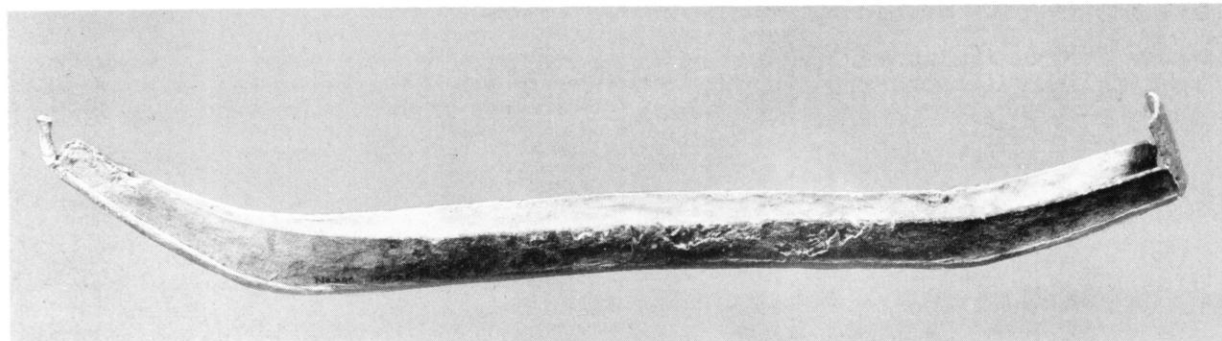
It remains to be added that the isotopic composition of the lead in various ores differs because some of the atoms of lead 206, lead 207, and lead 208 are formed respectively by the radioactive decay of uranium 238, uranium 235 and thorium 232. Different ores will have a different lead isotope composition depending on the geological age and on the relative amounts of uranium and thorium initially present in the ore-forming fluids.

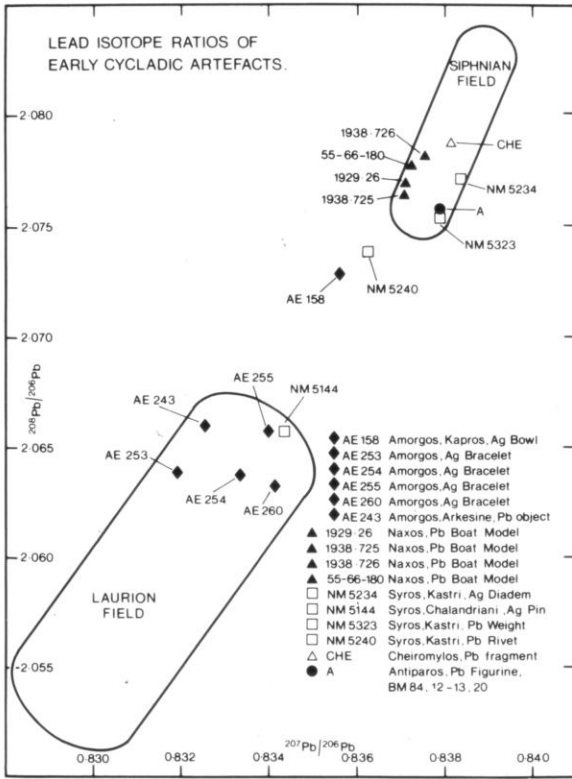
Work at Oxford

This method of provenancing metals has been applied at Oxford with great success to locating the sources of lead and silver in the Bronze Age Aegean and to ancient sources of copper. In fact the isotopic composition of lead in a particular ore deposit is not quite constant, but analyses of a number of samples from a deposit define a fingerprinting "field" of composition.

Early Bronze Age culture of the Cycladic Islands of the Aegean made use of lead and silver. Lead isotope analyses made at Oxford of four lead boat models dating to about 2900 BC, which were found in a grave on Naxos, fall in the isotopic field characteristic of the lead-silver ores from the mines on the island of Siphnos (see IAMS Newsletter No.4, p.3).

This was first proof that the Siphnos mines were





Lead isotope ratios for 3rd millennium silver and lead objects from the Cyclades compared with the isotopic fields characteristic of the Siphnian and Laurion mines. The data provides evidence that both regions were exploited for silver in the Early Bronze Age

originally exploited in the Early Bronze Age, and this was later confirmed by C-14 dating. A number of other Early Cycladic silver and lead objects, found mostly on Amorgos, fall instead in the Laurion field, proving that these mines also were first worked in the 3rd millennium BC and that the metal from them was used by the Cycladic people.

Byproduct of copper

The lead isotope method has now been applied to shed light on an aspect of metallurgy in the Timna Valley, in Israel, which has so far not been widely publicised: the possibility that iron may have been produced in small quantities there as a byproduct of copper.

Professor Rothenberg first found iron bracelets at Timna in 1964 when excavating one of the big smelting camps – Site 2, the now famous “Mushroom” camp. Four years later during the excavation of the Egyptian-built mining temple, which dates to the 12th century BC, more iron objects were found: iron lumps and rock fragments, and also several well made finger rings, one with clear remains of gilding.

As elsewhere at this time, iron was still regarded as a rare metal and used chiefly for jewellery; indeed, five hundred years before the Egyptian miners built their temple at Timna, an Akkadian text recorded that iron was worth eight times as much as gold.

Analyses of Timna’s iron objects by Professor Bachmann, and at Oxford, show by the absence of nickel that they were made of smelted, not meteoritic, iron. The same analyses show copper concentrations in the iron of from 0.1 to 2 per cent.

It had long been suspected that the earliest smelted iron might have been accidentally produced in a copper smelting furnace. One clue was the knowledge, since extensive analyses made in Stuttgart in the 1960s, that ancient copper often contains large amounts of iron – a phenomenon which later received particular attention for the Late Helladic bronze at Nichoria in Greece.

Iron minerals were usually present in the charge of an ancient copper smelting furnace, either as an unwanted part of the copper ore, or added in order to flux siliceous copper ores like those at Timna. Though most of the iron passes as oxides or silicates into the slag, experimental work both by Rostoker and Tylecote has shown that under certain conditions some may be reduced to the metallic state and incorporated into the copper metal.

Dr Craddock’s analyses of copper artefacts found in the Timna temple show that many contain up to 2 per cent, and some up to 7 per cent, of iron. Professor Tylecote has demonstrated by experiment that this iron may be removed from the copper by a refining process in which the impure copper is kept molten for some hours in a crucible. Under the right reducing conditions the iron separates out as an upper layer which is sufficiently malleable to be forged into simple objects such as rings.

Temple jewellery was iron from Timna

Many of the votive gifts found in Timna were actually brought from Egypt by the mining expeditions; and those that bore hieroglyphic inscriptions and cartouches have enabled the temple to be accurately dated. As a few iron objects are known from Egypt in the Late Bronze Age, it was reasonable to suppose that the iron jewellery found among the treasures could have been of Egyptian origin.

Comparative lead isotope analyses of copper and iron ores from Timna, together with the iron jewellery, show that this was not the case. The iron objects have the same lead isotope fingerprint which characterises the Timna ores and the few Timnian copper artefacts so far analysed. The iron jewellery here is clearly a local product. The other strands of evidence summarised above suggest strongly that the metal from which the jewellery was made was a rare and accidental byproduct of copper smelting and refining at Timna.

Lead isotope analysis has thus helped to clear up one of the major mysteries of Timna’s ancient mining: it may well prove to be the tool to solve other important puzzles surrounding the emergence of iron as one of man’s most useful materials.

Lead isotope ratios for metal ores from Timna compared with the isotopic compositions of copper objects and iron jewellery found in the Egyptian mining temple nearby

