

## Determining Prehistoric Mining Practices in Southeastern Europe Using Copper Isotopes

Wayne Powell (1), Ryan Mathur (2), H. Arthur Bankoff (1), Aleksandar Bulatović (3), and Vojislav Filipović ( )

(1) Brooklyn College, City University of New York, Brooklyn, United States , (2) Juniata College, Huntingdon, United States , (3) Arheološki Institut, Srpska Akademija Nauka i Umetnosti, Belgrade, Serbia

Copper was first smelted from malachite at 5000 BCE in Serbia. There the Eneolithic (Copper Age) began with the production of small jewelry pieces and progressed to the casting of massive copper tools near its end, approximately 2000 years later. However, copper metallurgy in southeastern Europe ceased or significantly decreased in the later third millennium, several centuries before the Bronze Age began. Whether this metallurgical hiatus was the result a cultural shift or depletion of natural resources remains an ongoing subject of debate.

It has been speculated that the marked reduction in metal production at the Eneolithic-Bronze Age transition was due to the exhaustion of surficial weathered oxide ores and the technical inability to smelt the underlying sulfide minerals. The behavior of copper isotopes in near-surface environments allows us to differentiate highly weathered oxide ores that occur at Earth's surface from non-weathered sulfide ores that occur at greater depth. The oxidation of copper generates fluids and associated minerals that are enriched in the  $^{65}\text{Cu}$  isotope. Thus, oxidative weathering of sulfide ores leads to the development of three stratified isotopic reservoirs for copper: 1) oxides above the water table that are enriched in  $^{65}\text{Cu}$ ; 2) residual weathered sulfides minerals at the water table that are depleted in  $^{65}\text{Cu}$ ; and 3) non-fractionated, non-weathered sulfide ore below the water table. And so, the transformative shift to sulfide-based metallurgy will be delineated by a significant decrease in  $\delta^{65}\text{Cu}$  in copper artifacts corresponding to the first use of  $^{65}\text{Cu}$ -depleted residual ore.

The degree of variability of primary ore composition from numerable ore deposits would likely result in the overlap of copper isotope composition between populations of artifacts. Therefore, shifts in the mean copper isotope values and associated standard deviations would best reflect changes in ores use. A baseline value of  $-0.2\text{‰} \pm 0.5$  (1 [U+F073]) was determined from an average of 164 published measurements from chalcopyrite and bornite from 8 epithermal and massive sulfide deposits. Twenty-two (88%) of Eneolithic artifacts (n=25) have values greater than this, whereas eight (73%) of the Early Bronze age artifacts (n=11) yield compositions less than  $-0.2\text{‰}$ . The mean of Middle Bronze Age, Late Bronze Age and Early Iron Age (n=86) cluster near  $-0.2\text{‰}$ . This pattern is consistent with a progression to the mining of ore assemblages from increasing depths through prehistory.

The shift from  $^{65}\text{Cu}$ -enriched to  $^{65}\text{Cu}$ -depleted copper in artifacts across the Eneolithic-Bronze Age boundary at 2500 BCE indicates that accessible near-surface oxide ore reserves were depleted after approximately two millennia of mining, and that the beginning of the Bronze Age in the Balkans corresponded to the acquisition of pyrotechnology which allowed for the extraction of metals from sulfide minerals and the resumption of copper mining activity in the region.