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Andean Ores, Bronze Artifacts, and Lead Isotopes: Constraints on Metal Sources in Their Geological Context

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Abstract

With a focus on bronze production in the south-central Andes during the Middle Horizon, this study reports the first archaeological use of lead isotope analysis to investigate metallic ores and metal artifacts in the Andean zone of South America. Because the vast majority of metal deposits in the Andean cordillera formed in a convergent plate boundary setting, lead isotope compositions of most Andean ore sources are not unique. Lead isotope ratios of central and south-central Andean ores define four geographically distinct ore lead isotope provinces, oriented and elongated parallel or sub-parallel to the trend of the Andean cordilleras. Consequently, ore lead isotope ratios vary strongly from west to east along transects through the coast, highlands and altiplano, but they exhibit much less variation from north to south. The strong west-to-east variation in ore lead isotope signatures allows discrimination between ore bodies, and ultimately between metal artifacts, as a function of macro-ecozone location: coast, junga-qiswa, puna, altiplano. We present the most up-to-date database of ore lead isotope signatures for the south-central Andes including those determined for ores we sampled over an approximate 250,000 km sq region within Bolivia, N. Chile, and NW Argentina. Lead isotope signatures of Cu-As-Ni bronze artifacts from Tiwanaku (altiplano capital) and San Pedro de Atacama (desert oasis entrepôt) establish that altiplano and high sierra ore bodies provided the metal for both assemblages. Conchopata (Wari) arsenic bronze artifacts exhibit lead isotope ratios compatible with the Julcani (Huancavelica) copper sulfarsenide deposit.

Keywords: lead isotopes, isotope provinces, metal sources, convergent plate boundaries, Andean metallic ores, Middle Horizon bronzes
Introduction

The utility of lead isotope analyses for determining the geologic sources of archaeological raw materials depends heavily on the availability of lead isotopic data for those geologic sources. The integrity of interpretations is greatly enhanced when the geologic context of the ore analyses and the strengths and weaknesses of the ore lead isotope database are taken into account. We present the geological framework of lead isotope signatures determined for Andean ore deposits and use the most current available database to discuss the implications of this framework for the application of lead isotope ore and artifact analyses to the study of Andean metallurgy in prehistory. Considering the strengths and limitations of the lead isotope analytical method in archaeological contexts, we suggest ways in which prospective future studies pertinent to archaeology may be framed and pitfalls avoided. Case studies that utilize lead isotope data determined for artifacts from Conchopata, a Middle Horizon, central Andean site, and from the south-central Andean sites Tiwanaku, San Pedro de Atacama, and Pulacayo consider the implications of the research results in the context of the Andean ore lead isotope database.

The ability to determine the source(s) of Andean ores from which metal was extracted to manufacture objects in prehistory offers archaeologists the potential to discriminate whether ancient metalworkers used local materials or exploited ores from significant distances. Ore source identification also aids in reconstructing trade routes and exchange patterns. Lead isotope tracer analysis is the most effective means currently employed to link a metal artifact to its source ore. Small variations measured in the isotopic compositions of copper and iron caused by kinetic mass fractionation potentially could shed some light on the sources of these metals in ores, but these studies are in an initial stage as applied to ore genesis (e.g., Markl et al. 2006; Mathur et al. 2009). Further, the isotope ratios of these relatively light elements are much more likely to be
fractionated by weathering and ore processing than those of lead. Isotope ratios of osmium show large variations in nature due to radiogenic decay. Since osmium is a platinum group element, however, it does not share the transport chemistry and deposition mechanisms of lead, copper, silver and zinc, and the existing database of ore analyses utilizing osmium isotopes is small. By contrast, publications of several hundred lead isotope analyses of Andean ores are available.

Lead from different geologic sources varies isotopically according to the ages and geologic histories of those sources, and the general geological provenance of the lead in an ore can be deduced from its lead isotope ratios. Lead commonly occurs together with ore minerals of copper, silver, zinc and tin, either as galena (PbS) or as a trace constituent in minerals of the other metals. This reflects the fact that lead is transported in ore-forming solutions by the same chemical complexes and deposited by the same mechanisms as these other metals (e.g., Wood et al. 1987). Lead isotope ratios thus reflect not only the geological sources of the lead itself, but to some extent those of other metals as well.

Mass spectrometers can produce precise lead isotope measurements with only a few tens of nanograms of lead from a sample, thus sample size is rarely a concern. The large kinetic fractionation effects measured in the isotopes of lighter elements, such as oxygen and sulfur, are not observed in the lead isotopes because of their large masses and the small mass differences between them. For instance, loss of at least 80% of the lead in an ore during ore roasting would be required to shift the lead isotope ratios enough for the difference to be measured by thermal ionization mass spectrometry (Macfarlane 1999a; Cui and Wu 2011). Evaporation of lead, as would occur during roasting and smelting of ore, fractionates lead isotopes to such a minute degree as to be within the range of isotopic variability of even an isotopically homogeneous source ore deposit (Cui and Wu 2011), so that the lead isotopic composition of an artifact will
reflect faithfully that of the lead in the materials used to make the artifact.

**Lead isotope ratio studies of archaeological metal artifacts**

Lead isotope ratios have been used for many years to identify the sources of metal ores used in the production of artifacts with provenience in the eastern Mediterranean region (e.g., Yener et al. 1991; Sayre et al. 1992; Stos-Gale et al. 1995). In order to characterize the isotopic composition and variability of each ore source as completely as possible, these studies have often used a statistical approach based on multiple, successive lead isotope analyses of individual ore bodies. The lead isotopic compositions of artifacts are then compared with isotopic fields determined for the ore sources (Sayre et al. 1992; Stos-Gale et al. 1995). It is implicit in this approach that, given enough data of sufficient precision, the lead isotopic composition of an artifact may be matched with a unique metal ore source. Following this assumption, these studies have usually relied only on the most precisely determined lead isotope ratios, those of $^{207}\text{Pb}/^{206}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$.

Although the exclusion of ratios involving the low-abundance, stable $^{204}\text{Pb}$ isotope improves the precision of the data, it also removes some of the natural geological variability of the data. For example, fields of ore analyses which are clearly separate in plots involving $^{204}\text{Pb}$ may overlap markedly in plots of $^{208}\text{Pb}/^{206}\text{Pb}$ vs $^{207}\text{Pb}/^{206}\text{Pb}$ (Yener et al. 1991). Ignoring $^{204}\text{Pb}$ sharply limits the ability to relate ore and artifact lead isotope data to the variability of lead isotopes in their geological context. The $^{206}\text{Pb}$, $^{207}\text{Pb}$ and $^{208}\text{Pb}$ isotopes are all increasing with time at different rates depending on the parent/daughter values of their sources. For example, a diagram based on the $^{208}\text{Pb}/^{206}\text{Pb}$ ratio cannot show whether variations arise
from the thorium-derived $^{208}\text{Pb}$ component or the uranium-derived $^{206}\text{Pb}$ component or some combination. By plotting each radiogenic isotope as a ratio with the stable $^{204}\text{Pb}$ isotope, the individual variations of each parent/daughter system can be seen. Studies examining the geographic variability of lead isotope ratios of potential ore sources and the geological causes of variability, as well as making use of ratios involving $^{204}\text{Pb}$ (e.g., Stos-Gale et al. 1997) promise a broader and more sound understanding of the significance of lead isotope ratios in artifacts.

Ores from different geographic areas of the Andes, one of the world’s great copper- and silver-producing regions, have different isotope compositional ranges, reflecting different geological sources of lead (Macfarlane et al. 1990; Kamenov et al. 2002). Ores from some areas of the Andean zone also exhibit very low isotopic variability over long distances, especially for deposits distributed parallel to the general north-south trend of the Andes mountain ranges. One consequence of this phenomenon is that, no matter how well characterized the lead isotope ratios of an Andean ore source may be, the isotopic compositions of most Andean sources are not unique. The work of Albarède et al. (2012) introduced a method of deriving variables from the lead isotopic compositions of ores that is potentially useful in describing the ore lead isotopic variability of geologically complicated areas. The authors used this method to distinguish Spanish coins derived from Mexican and Peruvian ore sources. Smelted metals with identical lead isotopic compositions, however, are still not distinguishable by the Albarède et al. model. This poses a serious problem for simple attempts to match artifact compositions to ore sources. In addition, many Andean ore deposits have fairly homogeneous lead isotope ratios, but others show significant internal variability resulting from heterogeneity in the ore metal sources themselves.
The geologic context of Andean ore deposits

The vast majority of metal ore deposits in the Andean cordillera formed within the last 70 million years in a convergent plate boundary setting. Figure 1 presents a simple representation of this plate boundary, where the Pacific ocean seafloor and its immediately underlying mantle (known geologically as the Nazca Plate; see Fig. 2) converge with the South American plate, which consists of the continental crust of South America and its immediately underlying mantle. The seafloor plate, being denser on average than the adjacent continental margin due to its basaltic composition, passes under the continental crust into the deeper mantle, a process called subduction. For most of the length of the Andean convergent boundary, it appears that virtually all of the sediments on the seafloor are being subducted into the mantle. There is evidence that the Nazca plate has even abraded the western edge of South America causing additional continental crust to be subducted (Stern 1991).

The process of subduction has formed a narrow and deep (8065 m) trench, known as the Peru-Chile Trench (Figure 2), in the Pacific Ocean, 160 km from the western margin of South America, following the coastlines of Peru and Chile. The Peru-Chile Trench marks the surficial geological boundary between the Nazca Plate to the west, which forms the southeast ocean floor of the Pacific Ocean, and the South American Plate to the east. The presence of the trench has impacted profoundly the near-shore, coast, and foothills environments of the western slopes of the Andean cordillera, with major consequences for the economic and political development of societies utilizing and inhabiting these zones in prehistory. The location and trajectory of the trench can also be understood as bearing a relationship to the lead isotopic provinces that have been determined for metallic ore bodies in the central and south-central Andean zone (Macfarlane et al. 1990).
As the seafloor plate is subducted into the mantle, its basaltic lavas and seafloor sediments are subjected to increasing pressure and heat causing them to give off water and water-soluble elements. The release of these components from the subducting plate into the overlying hot mantle at depths of \(\approx 100-150\) km causes that mantle to melt partially, and the magmas generated above the downgoing slab rise up into and in some cases through the overlying continental crust. Subduction thus produces zones of volcanic activity, called volcanic arcs (see Fig. 1), along the edges of overriding plates virtually everywhere that tectonic plates converge.

The chemistry of magmas formed at convergent boundaries has been the subject of decades of intensive study, because they represent the primary mechanism of growth of the continents over the history of the Earth (see, e.g., Gill 1981). These magmas start out, in their source regions, as melts derived from the mantle overlying the downgoing slab mixed with water and water-mobile elements from the subducting slab and sediments. As these magmas rise into the old, chemically and isotopically heterogeneous continental crust, they melt and assimilate material from that crust to varying degrees, which modifies their chemistry. It is often thought that, other factors being equal, the thicker the continental crust an arc magma must pass through, the more of that crust it will incorporate, and the more its chemistry will be modified.

Hydrothermal activity related to the emplacement of convergent boundary magmas along the western margin of South America has been responsible for the formation of most metal ore deposits in the Andean cordillera, including such giant deposits as Chuquicamata and Collahuasi (N. Chile), El Salvador (Central Chile) and Potosí (Bolivia). As magmas containing dissolved water rise into the upper crust they produce fluids rich in dissolved chloride, sulfur species, and metals. These fluids permeate, react with, and promote fracturing of the surrounding rocks, producing hydrothermal alteration and metal mineralization of various kinds. The heat from the
magma also causes circulation of fluids in the shallow crustal rocks, and these fluids mix with the metal-bearing magmatic brines and also participate in the formation of ore deposits. Lead isotope ratios can reveal which components of the geological environment have contributed the majority of lead to the ore.

**Ore lead isotope systematics**

The abundances of lead isotopes in rocks change slowly over geologic time scales due to the decay of parent isotopes of uranium and thorium to stable daughter isotopes of lead: $^{238}\text{U} \Rightarrow ^{206}\text{Pb}$, with a half-life of 4.5 billion years; $^{235}\text{U} \Rightarrow ^{207}\text{Pb}$, with a half-life of 700 million years; and $^{232}\text{Th} \Rightarrow ^{208}\text{Pb}$, with a half-life of 14.1 billion years.

The relative abundances of lead isotopes in rock samples are thus a function of the ages of the rocks and the relative abundances of U, Th, and Pb in the rocks. In the geological literature, lead isotope abundances are reported as ratios relative to the stable isotope $^{204}\text{Pb}$, so that the growth of each radiogenic isotope in response to its specific parent may be seen independently. Ratios are typically plotted on diagrams of $^{207}\text{Pb}/^{204}\text{Pb}$ vs. $^{206}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb}$ vs. $^{206}\text{Pb}/^{204}\text{Pb}$.

A number of geologic processes fractionate U, Th and Pb from one another and produce rocks with different U/Pb, Th/Pb and U/Th ratios. Over time these differences produce lead isotope variability in the Earth. For example, when rock melts to form magma in the Earth, uranium generally partitions into the melt and away from the residue, so that when the magma solidifies the resulting igneous rocks have higher uranium and U/Pb values than the magma source region. Since the rocks of the continental crust are made up of materials derived from at least one episode of melting, the continental crust generally has higher U/Pb than the mantle, and
this has led to the evolution of crust with higher $^{206}\text{Pb}/^{204}\text{Pb}$ and $^{207}\text{Pb}/^{204}\text{Pb}$. Uranium is also much more mobile than thorium in aqueous fluids. For example, metamorphism of rocks drives water out of them, and uranium tends to be lost from the metamorphic rock together with the water, while thorium remains (Gray and Oversby 1972). This produces a substantial decrease in the U/Th value of rocks which have been strongly metamorphosed. Rocks which have had high U/Pb ratios for a long period of time will have elevated $^{206}\text{Pb}/^{204}\text{Pb}$ and $^{207}\text{Pb}/^{204}\text{Pb}$, and those which have had high Th/Pb will have elevated $^{208}\text{Pb}/^{204}\text{Pb}$. Igneous rocks, and ores produced as byproducts of igneous activity, will have lead isotope characteristics inherited from the materials that underwent melting to form the parent magmas.

Lead isotope evolution in the Earth may be thought of in terms of four major isotopic reservoirs, as modeled by Doe and Zartman (1979) (Fig. 3). The first reservoir is the Earth’s mantle and the oceanic crust (labeled a in Fig. 3), which is produced by melting in the mantle at divergent plate boundaries. The mantle becomes depleted in uranium and thorium by the melting and extraction of magmas over time and evolves along a track of relatively slow increase in the radiogenic isotopes. The second reservoir is the upper continental crust (labeled c in Fig. 3). The upper continental crust is the repository for uranium- and thorium-rich products of melting, thus it has evolved more rapidly to higher values of $^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb}$. The third reservoir, the lower continental crust (labeled d in Fig. 3), consists of the high-grade metamorphic rocks which make up the deeper levels and central parts of the continental cores. Rocks of the lower crust have lost uranium relative to thorium and lead during high-grade metamorphism, and may be older than 2 billion years. Over time, the lower crust develops a distinctive signature with very low $^{206}\text{Pb}/^{204}\text{Pb}$ and $^{207}\text{Pb}/^{204}\text{Pb}$, owing to the loss of uranium,
but more normal $^{208}\text{Pb} / {^{204}}\text{Pb}$ due to retention of thorium. The final major reservoir is the orogene (designated b in Fig. 3), where material from all of the other reservoirs is mixed to produce magmas that are added as new growth to the convergent continental margin.

In the Doe and Zartman (1979) model, these four reservoirs are presumed to have interacted periodically to generate new continental crust in the orogene, and the isotopic evolution of each reservoir through time is modeled in a stepwise fashion (see Fig. 4; Zartman and Doe 1981)). This model, although simplistic especially where internal processes in the lead-poor mantle are concerned, has proven a generally useful way of understanding the lead isotopic evolution in the Earth and the continental crust.

Figure 5 shows the Zartman and Doe (1981) model curves in relation to the measured and available lead isotopic compositions of Andean rocks. The subducting seafloor (reservoir a in the Doe and Zartman model) corresponds to the Nazca plate, which is composed of basaltic lavas derived by partial melting of the mantle and the underlying uppermost mantle. Unfortunately, only six lead isotope measurements published more than 30 years ago are available for the Nazca plate (the area labeled “Nazca seafloor” in Fig. 5), and these samples are from a site off the coast of northern Peru (Unruh and Tatsumoto 1976). These analyses have higher $^{206}\text{Pb} / {^{204}}\text{Pb}$ and $^{208}\text{Pb} / {^{204}}\text{Pb}$ than predicted by models, but they still have lower $^{208}\text{Pb} / {^{204}}\text{Pb}$ than any Andean ore measured to date.

The upper continental crust (reservoir c) is represented by two groups of rocks exposed in the Andean cordillera (Macfarlane et al. 2001; Kamenov et al. 2002). The rocks labeled “high $^{206}\text{Pb} / {^{204}}\text{Pb}$ source” in Figure 5 include low-grade metamorphic rocks and sedimentary rocks in northern Chile, southern Bolivia and NW Argentina, which correspond very closely to the upper crust curve (Fig. 4, curve c) of Zartman and Doe (1981). The upper crust reservoir also includes
the thick sequence of Paleozoic shales and siltstones that outcrop extensively in the eastern altiplano and Cordillera Real (labeled “Paleozoic sedimentary rocks” in Figure 5). These have lower $^{206}\text{Pb}/^{204}\text{Pb}$ and higher $^{208}\text{Pb}/^{204}\text{Pb}$ ratios than the other upper crustal rocks, indicating a higher Th/U value in their source than occurs in the Zartman and Doe (1981) model of the upper crust (Fig. 4).

The lower crust (Fig. 3, reservoir d) is represented by ancient, high-grade metamorphic "basement" terranes, some produced by metamorphism as much as 2 billion years ago. These terranes outcrop at the surface in some areas of the central Andes and are known elsewhere from drill cores and from fragments brought up by volcanic eruptions. These rocks generally exhibit low U/Pb ratios due to loss of uranium during metamorphism and, therefore, correspond closely to the Zartman and Doe (1981) “lower crust” curve (Fig. 4, curve d) with low $^{206}\text{Pb}/^{204}\text{Pb}$ relative to the orogenic $^{208}\text{Pb}/^{204}\text{Pb}$ value (the field labeled “low $^{206}\text{Pb}/^{204}\text{Pb}$ source” in Fig. 5).

The orogene reservoir of Doe and Zartman (1979) is represented in the Andes by the igneous rocks produced at the convergent plate boundary (Fig. 3). These rocks originate in the mantle as partial melts containing lead from the mantle and from subducted seafloor sediments, and they incorporate additional lead from lower and upper crustal rocks as they rise and are emplaced in the crust. Because the mantle contains very little lead, the isotopic signature of its contribution to the mixture is quickly overwhelmed. These magmas thus incorporate lead from the continental crust initially in the form of subducted seafloor sediments, which are dominated by the upper crustal component and are somewhat homogenized by the processes of erosion, transport, and sedimentation, and later by melting and incorporation of specific rocks in the continental crust as they rise into it and are emplaced. Thus the orogene reservoir serves to remix
materials from the other three reservoirs. Representative Andean orogene rocks from the Lima segment of the Peruvian coastal batholith are plotted in Figure 5 and form a small field near the modern end of the Zartman and Doe orogene curve (Fig. 4).

**Andean ore lead isotope provinces**

Lead isotope ratios of ore deposits in the central and south-central Andean zone display a distinctive, large-scale pattern which reflects the interaction of the major lead reservoirs in the crust and mantle in the generation of metal ores, as outlined above (Macfarlane et al. 1990; Aitcheson et al. 1995; Tosdal et al. 1999; Macfarlane et al. 2001; Kamenov et al. 2002; Albarède et al. 2012). This pattern is defined by four geographically distinct ore lead isotope provinces, shown in Figures 6 and 7 (provinces I, II, IIIa and IV), and a fifth compositional group which does not define a geographically coherent province (province IIIb).

**Province I - the orogene source**

Ore deposits in Chile, including those located on the western slopes of the Andes range, exhibit a remarkably low variability of lead isotope ratios over a wide area, despite variations in the age, thickness, and geologic character of the crust. This area, designated province I (Macfarlane et al. 1990; Macfarlane et al. 2001; Kamenov et al. 2002), extends along the western margin of South America from about 34°S latitude to approximately the Chile-Peru national border, where it is interrupted by ores with different isotopic characteristics (see Fig. 6). Province I reappears at about 15°S latitude and continues along the coast of Peru to roughly Peru’s border with Ecuador. Province I corresponds well to the isotope composition of orogene lead (curve b in Fig. 4; Zartman and Doe 1981) and also to a weighted average of the isotope compositions of Nazca plate sediments (Macfarlane 1999b). Because the mantle itself contains little lead, addition of subducted sediments and fluids to the mantle source region would
rapidly dominate the lead isotope composition of the orogene source. The isotopic homogeneity of the province I ores, their correspondence with Nazca plate sediments, and their lack of correspondence with any known, exposed Andean crustal rocks all suggest that province I is dominated by a well-mixed orogene source (see Fig. 8; Barreiro 1984; Aitcheson et al. 1995; Macfarlane 1999b).

Province IIIa - Paleozoic sedimentary rock upper crustal source

To the east of province I lies a large highland (sierra) region where the ores have consistently higher $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb}$ values than are characteristic of province I. This region is designated lead isotope province IIIa (see Fig. 8; Macfarlane et al. 1990). Lead isotope ratios of ores from province IIIa require a source with a history of higher U/Pb and also higher Th/U ratios than occur in the orogene source of province I. Province IIIa is also displaced towards higher $^{208}\text{Pb}/^{204}\text{Pb}$ values than appear in the upper crust curve of Zartman and Doe (1981) and is therefore associated with an upper crustal-type lead source with a higher Th/U value than in the Zartman and Doe model. Lead isotopic variability within province IIIa is much greater than within province I (e.g., $^{206}\text{Pb}/^{204}\text{Pb}$ varies from about 17.9 to 19; see Fig. 8), which is consistent with derivation of crustal lead by melting of heterogeneous, radiogenic upper crustal rocks in individual ore-forming systems, rather than by the addition of relatively homogenized subducted sediment to the magma source, as occurs in province I.

Unique among the lead isotope provinces, province IIIa includes several deposits much older than Cenozoic age (> 65 million years). Because most metal ore minerals, especially sulfides, have much lower U/Pb and Th/Pb ratios than typical crustal rocks, the lead isotope ratios of ore minerals change little after they form (or not at all in the case of galena). The source rocks of ore metals, whether they are part of the continental crust or of the sub-Andean mantle
wedge, have higher parent/daughter isotope values and continue to evolve isotopically through
time. Therefore, ores which form at widely different times from the same geological source will
have different lead isotope compositions, and those compositions will be related to each other by
the age differences between the deposits and the parent/daughter values of the source. The longer
the time difference between formation, the more different the ore lead isotope composition will
be. Ores in province IIIa appear to demonstrate this relationship.

The oldest ore deposits in province IIIa are thought to be of Ordovician age (415-490 Ma)
and include the Aguilar and Helvecia mines in NW Argentina (see Figs. 6 and 7). The Cobres
copper deposit, also in NW Argentina (see Figs. 6 and 7), is not well dated but is associated with
Ordovician age intrusive rocks and is probably of this age as well. Lead isotope analyses of ores
from these deposits cluster in and define the lower end of the province IIIa lead isotope array.
The middle section of the province IIIa array is dominated by deposits of Mesozoic age (≈ 180-
211 Ma) (Evernden et al. 1977), including the Don Carlos and Chojlla deposits on the Bolivian
altiplano (see Figs. 6 and 7). The upper end of the province IIIa array is defined by many
analyses of late Tertiary deposits, most younger than 30 Ma, including those at Potosí, Porco,
Pirquitas, Pulacayo and Concordia, located on the more southerly reaches of the Bolivian
altiplano (see Figs. 6 and 7). Taken together, these data suggest that lead in the province IIIa ores
is derived from a common source with Pb isotope ratios and U/Pb and Th/Pb values typical of the
upper crust continental compositions.

Province II - mixing of orogene (pl) and upper crustal (pIIIa) sources

Another lead isotope province, most prominently seen in the high cordillera of Peru, is
province II. Samples from individual ore deposits in province II define arrays between the fields
of province I and province IIIa ores (see Fig. 8) and appear to represent mixing between the
province I orogene source and the upper crustal province IIIa source. To form such an isotopic array, lead from the two sources must not mix completely with each other before the geological formation of the ore minerals. Mixing of different sources thus probably took place at or near the site of ore formation. One scenario consistent with this constraint would involve a magma containing province I type lead, which rose rapidly through thick continental crust and only assimilated or hydrothermally leached a significant amount of continental crust close to the surface, near the level where it would solidify and create ore deposits.

Province IV- Lower crustal sources with orogene input

The fourth Andean lead isotope province extends from the southern coast of Peru into the western altiplano and Lípez region of southern Bolivia (see Figs. 6 and 7). Ores in this area, designated province IV, have low $^{206}\text{Pb}/^{204}\text{Pb}$ and $^{207}\text{Pb}/^{204}\text{Pb}$ values compared to $^{208}\text{Pb}/^{204}\text{Pb}$ ratios and form a broad array in lead isotope ratio diagrams extending from the province I field towards lower values of $^{206}\text{Pb}/^{204}\text{Pb}$ (see Fig. 8). Province IV ores represent varying amounts of mixing between a province I orogene-type source and the ancient, high-grade metamorphic basement rocks which represent the lower crust component beneath much of the central Andes.

Geologic studies of high grade metamorphic rocks in the central Andes indicate that they comprise distinct terranes which have been affected by magmatic and metamorphic events ranging from 400 million years ago to more than 2 billion years ago (Loewy et al. 2004). This diverse geologic history has produced strong isotopic heterogeneity and variability in these metamorphic basement rocks. The great majority of them, however, have the low $^{206}\text{Pb}/^{204}\text{Pb}$ values appropriate to representing the lower end member in the mixing scheme, and the average
of their modern lead isotope compositions is near the present day end of the lower crustal curve of Zartman and Doe (1981). Some ore deposits appear to contain lead dominantly from this lower crustal source, whereas others are moderately to slightly affected by it. Ores in province IV were probably generated by magmas that formed in the province I type source region above the subducting slab and then assimilated varying amounts of ancient metamorphic basement rock prior to mineralization. Areas where these low $^{206}\text{Pb}/^{204}\text{Pb}$ ore compositions occur are thought to indicate the overall extent of ancient, high-grade metamorphic basement rocks concealed beneath younger rocks in the central Andes (e.g., Tosdal et al. 1999).

Province IIIb - mixing of the orogene (pI) source with high $^{206}\text{Pb}/^{204}\text{Pb}$ upper crust

A final lead isotope province, designated province IIIb, includes ores with elevated values of $^{206}\text{Pb}/^{204}\text{Pb}$ relative to $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb}$ (see Fig. 8; Macfarlane et al. 1990). Data on low-grade metamorphic rocks in northern Chile and sedimentary rocks from northern Argentina (Gagnier et al. 1996; Egenhoff and Lucassen 2003) represent potential sources of province IIIb-type lead. The lead isotope characteristics of these rocks resemble very closely the upper crustal curve of Zartman and Doe (1981) (see Fig. 4). Unlike the other lead isotope provinces, province IIIb does not appear to form a geographically coherent region. Instead, there are small occurrences of this signature in both ores and volcanic rocks from southeastern Peru, northern Chile, and northwestern Argentina. This suggests the presence of relatively small enclaves of high $^{206}\text{Pb}/^{204}\text{Pb}$ metamorphic basement within the heterogeneous continental crust which have become involved in melting and ore formation.

The southern Altiplano/Lípez area

The Lípez area of southwestern Bolivia (see Fig. 9) has been poorly represented in previous lead isotope studies. New ore lead isotope data show that four of the lead isotope
provinces come together in this relatively small region, with lead isotope ratios of the ore deposits shown in Figure 10. Because so many ore deposits are represented in Figure 10, ores that group geographically are represented by the same symbols. Specific isotopic data for each deposit are presented in Table 1. Province IIIa ore lead compositions, which dominate further east and in the Cordillera Real, are represented mainly by deposits including Don Carlos, Corocoro and Pulacayo. The central altiplano, including deposits such as Avaroa, Carangas, Azurita and Chinchilhuma, contains geologically young deposits (mostly late Cenozoic) which plot at anomalously low $^{206}\text{Pb}/^{204}\text{Pb}$ for their age. This indicates the influence of lead from ancient, high grade metamorphic basement rocks that define province IV. The deposits most strongly affected by the underlying metamorphic rocks include María Luisa, Guadalupe, Negrillos and Carangas. Although these deposits overlap with the province IIIa array, they are all more than 400 million years younger than the corresponding IIIa deposits and cannot have formed from the province IIIa source. Less strongly affected province IV ores include Cobrizos, Bartola and Avaroa.

The Lípez region is also remarkable for the existence of several copper ores bearing the unambiguous lead isotope signature of province I despite their high elevations: these include Cerro Colorado, Inez, Eskapa, San Juan de Irismayu, Puca Mokho, and 25 de Julio. The existence of province I ore lead isotope signatures in this part of the Andes, at high elevation and in a region of very thick continental crust (>60 km) suggests either that these deposits formed before the crust thickened in the area or that the underlying crust itself is isotopically different from that further to the east. Sporadic occurrences of province IIIb lead isotope signatures at Taca Taca, Koholpani and Huancané (represented by a single analysis with very high $^{206}\text{Pb}/^{204}\text{Pb}$) do not form a geographically coherent province but appear to signal the local
involvement of high $^{206}\text{Pb}/^{204}\text{Pb}$ crust.

**Northwest Argentina**

Lead isotope ratios of ores from NW Argentina (Fig. 11) lie mostly within, and in part define, the range of province IIIa ore lead (Fig. 12). Older, Ordovician-age ores from the Aguilar, Helvecia and Cobres deposits contain lead with fairly homogeneous isotope ratios and $^{206}\text{Pb}/^{204}\text{Pb}$ near 18, which form a cluster well separated from the other province IIIa ores. Ores of intermediate, Mesozoic age including those from the Cari-Casini, Gigante, San Juan, Pumahuasi and Santana mines plot in the middle of the province IIIa array, and younger, Tertiary deposits plot at the high $^{206}\text{Pb}/^{204}\text{Pb}$ end of the province IIIa isotope array. Ore lead isotope variations within the Ordovician and Mesozoic deposit clusters are very small and compositions of different ore deposits overlap strongly. Although it is easy to tell the ores of these different ages apart from each other based on lead isotope ratios, it is not possible to differentiate among the ores within each group. Ores of Tertiary age, including those from the Capillitas, Concordia, Pan de Azúcar and Providencia deposits, plot in a larger area of the high $^{206}\text{Pb}/^{204}\text{Pb}$ end of the province IIIa array. Each of these Tertiary ore deposits defines a cluster distinct from the others, therefore, in addition to being isotopically distinct from the Ordovician and Mesozoic ore clusters, one can potentially distinguish among ores from individual deposits.

Consequently, the source of ore metal in an archaeological artifact having lead isotope ratios lying in the upper end of the province IIIa array may be identified potentially or ruled out on the basis of lead isotope ratios, whereas an artifact with compositions corresponding to the Ordovician or Mesozoic groups could only be generally identified with ores of that age.

In addition to ores within the province IIIa array, some NW Argentina ores have lead isotope characteristics outside the array. Ores from the Famatina/La Mejicana mine, for
example, form a tight cluster within the province I ore field, distinct from any other NW Argentina ores for which there are lead isotope data. Ore from the copper-rich Chorillos deposit plots slightly below the province IIIa array and at lower $^{206}\text{Pb}/^{204}\text{Pb}$ than the province I area, also isotopically distinct from any other NW Argentina ores. The Taca-Taca copper deposit has characteristics of province IIIb, with a large lead isotopic variability, which overlaps parts of province I, province IIIa and into the field of province IIIb. Many NW Argentina ores that have been analyzed for lead isotope ratios, including all of the Ordovician and Mesozoic ores except for Cobres, are from lead-silver mines that in some cases contain zinc, copper, or tin. Other deposits, including Cobres, Chorillos, Famatina/La Mejicana, Providencia and Taca-Taca, are primarily copper deposits.

**Applicability of the lead isotope ratio analytical method to identifying Andean sources of metallic ores used in the production of prehistoric artifacts: geological considerations**

In principle, the ore lead isotope variability that defines Andean lead isotope provinces can be used to constrain the source or sources of metals used in the manufacture of prehistoric artifacts. There are some significant qualifications. The most important limitation of the method stems from the fact that, in general, lead isotope signatures of ore deposits in the Andean zone are not unique. The very existence of any lead isotope province reflects the fact that ores distributed over a large area of the Andes share lead isotope characteristics and, as a result, these ores group within specific provinces. Ores in the same region that formed at about the same time from similar geological sources may have similar or identical ore lead isotope signatures. The subduction process can generate similar lead isotope compositions in ores on different continents. The Doe and Zartman (1979) model itself was originally constructed with data obtained from all over the world.
In the Andean zone, province I is especially homogeneous. The areal extent of province I, shown in Figures 6 and 7, is delimited by more than 100 lead isotope measurements from dozens of mining districts. As an example, an artifact with lead isotope ratios within the compositional range of ores from the huge, open pit mine at Chuquicamata (22°17’S, 3200 masl; see Fig. 9) would likely match just as well with ores from Collahuasi, the giant open pit mine in the high sierra of N. Chile (20°59’S, 4800 masl), or with ores from the El Salvador deposit in central Chile (26°15’S, 69°37’W; 2,300 masl), as well as ores from other deposits within province I. Disagreement between the lead isotope composition of an artifact and ores from a given deposit indicates that the lead in that artifact did not come from the deposit, but a match of lead compositions means only that the artifact could have been made from that ore or from other deposits in the same province. In provinces IIIa and IV, which exhibit much greater lead isotope variability, some deposits do not overlap isotopically with any other known deposits. A match of an artifact with one of these deposits would be much more strongly suggestive of ore source, but even then other deposits in the province not yet analyzed could also potentially provide a match.

The lead isotope provinces delimited in Figures 6 and 7 are elongated in the N-S direction, parallel or sub-parallel to the trend of the Andean cordilleras. This means that ore lead isotope ratios vary strongly from west to east along transects that cut across the Andean sierra and altiplano, but they exhibit much less variation from south to north, or in an orientation generally parallel to the trend of the Andes ranges. Another way of expressing this is that lead isotope ratios of metallic ore bodies in the central and south-central Andean zones vary considerably as a direct function of the distance of the deposit from the Peru-Chile Trench (see Fig. 2), and they vary also as a result of the geology of the South American continental crust. Within a given lead isotope province, ores located at roughly the same distance east of the trench
may have similar or identical lead isotope signatures, regardless of their relative distance apart in a N-S orientation parallel to the trend of the Andean ranges. In general, these isotopic variations reflect the increasing predominance of ore lead from the South American continental crust with increasing distance from the Peru-Chile Trench. The Collahuasi and Chuquicamata open pit copper mines provide an excellent example of this phenomenon (see Figs. 6 and 7 for the locations of these two giant deposits in N. Chile).

Consequently, in the Andean zone lead isotope ratios can be highly useful in distinguishing between sources located in the highlands and those in the coastal areas. They are less useful in distinguishing among sources that lie roughly along the prevalent trajectory of the Andean cordilleras and that are separated from south to north. Examples of these latter ore deposits are those located between central and northern Chile or between northwest Argentina and the Cordillera Real of Bolivia.

In addition, the lead isotope ratios of some provinces overlap with others. There is a substantial area in the center of Figures 6 and 7 where province IV overlaps with province IIIa. This overlap is less of a problem in geological studies, because the ages of the ore deposits are either known from radiometric dating or can be approximated from the geological context. These age determinations allow us to distinguish among different sources that contributed ore lead at different times. The method of Albarède et al (2012) offers a graphical means of discriminating among overlapping compositions of ores of different ages, albeit with the introduction of some model-based uncertainties. With the analytical methods currently available, however, the smelting process erases any information about the age(s) of the ore(s) used to extract the resulting metal. Thus, lead isotope ratios of artifacts that plot within the overlap areas of provinces IIIa and IV cannot be assigned unambiguously to either province. Moreover, the ore
source of an artifact formed from province II ores may not be identifiable unless the isotopic heterogeneity of the source ore is preserved in the smelted products and captured in the archaeological sampling. For example, smelting a province II ore could produce artifacts with homogenized signatures within either province IIIa or province I. Areas of ambiguity within which an artifact lead isotope analysis cannot be confidently assigned to a particular province are indicated in Figures 6 and 7.

Whereas the similarity of ore lead isotope ratios within a given isotopic province can frustrate efforts to link an artifact to a unique ore deposit, the existence of ore isotopic provinces can be highly useful in constraining the general geographic area from which the ore metal originated. Andean provinces I and IIIa lie parallel to each other on lead isotope ratio plots (Fig. 8), for example, but they do not overlap. Artifacts or groups of artifacts that plot consistently within the area of province I are highly unlikely to have been derived from province IIIa ores and vice-versa, even if a particular artifact cannot be matched directly with a specific ore deposit. Likewise, an artifact that plots within the non-overlapping area of province IV cannot have been produced from ores in provinces I or IIIa.

In regions such as the Bolivian altiplano there are numerous small, mineralogically similar copper deposits that could have been exploited by ancient miners, and it is impractical to sample and analyze them all. These miners may have used and exhausted small, high-grade ore bodies that have since been forgotten, or they may have used the surface outcrops of large ore bodies that have since been mined away. If the lead isotope ratios determined for an artifact plot within the isotopic range of a particular province, there is a high likelihood that the source ore occurred within the geographic bounds of that province, whether or not the specific ore deposit that was used by the ancient metalworkers has been sampled and analyzed.
Applicability of the lead isotope ratio analytical method to identifying Andean sources of metallic ores used in the production of prehistoric artifacts: archaeological considerations

The existence of lead isotope provinces having broadly similar ore lead isotope characteristics over large areas means that matching the isotope ratios of an artifact with a specific ore deposit is problematic. A match between an artifact and an ore body confirms that it is possible the artifact was made from that ore. If the ore was near the site where the artifact was retrieved, the case is more likely, but it remains possible that one or more other ore bodies in the same province supplied the metal. Lead isotope ratios may be used more confidently to rule out potential metal sources based on differences in isotope composition. If an ore has a very different lead isotope signature from that of an artifact with low lead content, it cannot have been a significant source of the metal in the artifact, and it may not have been used at all. If multiple artifact analyses do not show any overlap with a given ore, that ore may be ruled out as a source.

Confusion may arise when interpreting the lead isotope compositions of artifacts produced from a mixture of ores if one of the ore ingredients contains much more lead than the others. The lead isotope ratios of the alloy will reflect the composition of the lead-rich component, and others will be masked. For example, deposits of copper oxides, copper carbonates, and native copper of various sizes are widespread in the Andes today and were more widespread before modern mining removed the weathered, oxidized upper parts of many major deposits (e.g., those at El Abra, Collahuasi and Chuquicamata in N. Chile; see Figs. 6 and 7). Near-surface, oxidized copper deposits often form by weathering and dissolution of pre-existing copper minerals, usually sulfides, followed by reprecipitation from groundwater as copper carbonates, oxides, and native copper within meters or tens of meters from the surface. In most cases, lead is more mobile in this near-surface weathering environment and is carried away in
Although the lead isotope ratios of the resulting oxidized copper ores are not affected measurably by weathering, they often contain very little lead, however, on the order of parts per million or tens of parts per million. If, for example, such copper-rich, lead-poor ore were smelted to obtain copper, and that copper was alloyed with tin derived from an ore containing a percent or more of lead (such as a cassiterite ore that included small amounts of galena), the lead isotope ratio of the resulting tin bronze would be dominated by the lead from the tin ore, and the source of the copper in the alloy would be undetectable. If the copper and tin ores had widely differing lead isotope ratios and the lead in the resulting alloy was not dominated by either one, the lead isotope ratios of the resulting alloy would scatter between them, or even overlap with an unrelated ore.

This problem can be mitigated somewhat by first analyzing the lead content of the artifact, then measuring lead isotope ratios on samples with low lead concentrations. In principle, if a set of artifacts having generally low lead contents were formed from varying mixtures of two isotopically distinct ores, it should be possible to constrain the compositions of the two endmember mixing components using the lead isotope and lead concentration data. To our knowledge no one has tried to do this with South American artifact data.

The lead isotope compositions of artifacts can be used to identify the isotopic province the source ores came from. If the artifact isotope compositions lie well within the province I field, the upper Tertiary part of the province IIIa field, the province IIIb field, or the parts of province IV which do not overlap with province IIIa, the province of the ore source may be identified confidently. If the artifact compositions lie in the area of overlap between provinces IIIa and IV, the result is ambiguous, because the age of the source ore is not known. If the artifact
compositions form arrays overlapping provinces I and IIIa, mimicking the geological province II arrays, the result is also ambiguous. The artifacts could be made from ores from a province II deposit, or from a mixture of province I and IIIa ores, or the lead isotope signatures could conceivably reflect both possibilities. In other words, the mixing of province I and IIIa signatures could have taken place naturally during the formation of the ore deposit, or artificially during the production of the alloy. From lead isotope ratios alone there is no way to tell the difference.

**Bronze and the Andean Middle Horizon**

The development of bronze alloys in the central and south-central Andes occurred during the Middle Horizon (ca. CE 600–1000). Bronze production can be considered a technological marker of the Middle Horizon (Lechtman 1997, 2003a). During this horizon period communities throughout the Andes exploited metallic mineral deposits that were abundant, rich, readily accessible, and close by to provide three bronze alloy types that served local and state purposes: arsenic bronze, tin bronze, and a ternary copper-arsenic-nickel bronze alloy.

Bronze production during the Middle Horizon coincided with the establishment of the Wari state in the central Andean zone and the extensive Tiwanaku sphere of influence in the south-central Andean zone (Fig. 13). In both zones, bronze production was accompanied by the exploitation of new ore types that had not been exploited and smelted previously. Notable is the absence of exchange of these bronze alloy types between the two great spheres of production: Wari and Tiwanaku.

**The bronze divide**

In the south-central Andean region, dominated by the extensive and mostly arid altiplano, communities were able to satisfy their subsistence needs and requirements for non-local
materials, such as metallic ores, through elaborate, long distance exchange networks that were especially active and fluid during the Middle Horizon. Tin bronze, for example, was widely distributed via these north-south trending networks, but the networks did not reach farther north than the southern limits of Lake Titicaca. Artifacts of tin bronze have not been reported from Middle Horizon, central Andean sites. In contrast, it appears that arsenic bronze, produced commonly in the central Andes, was distributed either along the far north coast of present day Peru (Shimada 1985; Shimada and Merkel 1991) or via exchange routes that traversed the vertical Andean terrain from west to east. These highland routes normally did not penetrate farther south than Lake Titicaca.

During the Middle Horizon there appears to have been a divide (Lechtman 1979; Lechtman and Macfarlane 2006) between the types of bronze alloy produced and used within those interaction spheres influenced by Tiwanaku and those influenced by Wari. The reality of this divide can be tested by archaeological research and by materials and isotopic laboratory analyses of Middle Horizon bronzes and of ore bodies accessible to prehistoric Andean communities.

Goals of the study reported here

A primary aim has been to establish the range of copper ores accessible to Andean communities in each of the two Middle Horizon primary zones of bronze production and to establish a database of the lead isotope signatures of those ores. We focused primarily on ore bodies in the south-central Andean region (in Bolivia, Chile, and northwest Argentina), because lead isotopic coverage of copper ores and crustal rocks in the central Andes has been well published since the early 1990s (e.g., see Macfarlane et al.1990; Kontak et al. 1990; Tosdal et al. 1993, 1995). In contrast, prior to our study, lead isotope data were scarce for ores and rocks
located within the Bolivian Lake Titicaca Basin, on the Bolivian altiplano, and in the far southern Lípez province of Bolivia. Lead isotope data for ore bodies in northwest Argentina were largely unavailable, and even data for copper ores at well-known mine sites in northern Chile were often sparse.

A strong research focus lay in an effort to determine the “reach” of Tiwanaku with regard to the copper ore sources it accessed and the bronze artifacts produced within its sphere. We report here lead isotope ratio determinations measured for groups of bronze artifacts from sites within the Tiwanaku sphere and how we have attempted to relate those isotopic signatures to ore bodies from specific ecozones within the south-central Andean region. Our survey and ore collection regime covered an area of approximately 250,000 km² organized in four field campaigns from 1995 through 2006. The first scientifically excavated bronze artifacts from Tiwanaku and its neighbor Lukurmata resulted from the University of Chicago’s excavations from 1986 to 1994, led by Alan Kolata (Kolata, Ed. 1996, 2003). Lechtman’s materials analyses of many of these bronzes (Lechtman 2003a) led to questions about the varieties of ores utilized in their production and about the locations of those ores. A thorough and reliable database of south-central Andean copper ore bodies and their lead isotope signatures was critical to these inquiries.

A range of bronzes

The central Andean zone in prehistory coincides largely with what today are Peru and Ecuador, extending north from Lake Titicaca to the border of Ecuador with Colombia (Fig. 13). A metallic ore geological map of the central Andean zone (Lechtman 2003b, fig. 3) locates some of the world’s largest and richest copper sulfarsenide deposits in the central Andean sierra,
distributed within an ore field that extends from Pilzhum (Ecuador) in the north to Lake Titicaca. These deposits, containing sulfarsenide minerals such as enargite \([\text{Cu}_3\text{AsS}_4]\) and tennantite \([\text{Cu}_{12}\text{As}_4\text{S}_{13}]\) and their arsenate weathered products \([\text{e.g., chenevixite } \text{Cu}_2\text{Fe}_2(\text{AsO}_4)_2(\text{OH})_4\cdot\text{H}_2\text{O} \text{ and olivenite } \text{Cu}_2(\text{AsO}_4)(\text{OH})]\), would provide both copper and arsenic, together, to a smelting furnace charge. Smelting copper arsenate ores, or cosmelting the sulfarsenides with copper oxide ores (Lechtman and Klein 1999), produces copper-arsenic alloys directly.

Thus far, almost without exception, Middle Horizon bronze artifacts from the central Andean zone have been found upon analysis to be made from alloys of copper and arsenic (Lechtman 1981, 1997, 2005; Vetter et al. 1997; Bezúr 2003). On the basis of their mechanical behavior, Lechtman classifies as arsenic bronze those copper-arsenic alloys containing arsenic at a concentration of 0.5wt% or higher (Hosler et al. 1990; Lechtman 1996). Merkel and Shimada (Merkel et al. 1994) maintain that arsenopyrite \([\text{FeAsS}]\), which occurs plentifully in deposits only a few kilometers distant from Batán Grande, on the far north coast of Peru (Fig. 13), likely provided arsenic to the smelting furnaces at that Sicán (CE 850-1000), near-industrial, arsenic bronze production site. Central Andean artifacts made from arsenic bronze, whether from the far north Peruvian coast, the coast of Ecuador, or from the Peruvian highlands, tend to be small in scale: \textit{e.g.,} tupus, needles, spindle whorls, naipes (a Sicán-type, thin, sheet metal item), axe-monies, and cast, heavier objects that resemble digging stick points (Hosler et al. 1990; Vetter et al. 1997; Shimada 2000; Bezúr 2003).

The south-central Andes in prehistory includes Bolivia (Fig. 9); northern Chile, which today incorporates regions I (Tarapacá) and II (Antofagasta) as far south as approximately Taltal (25.26°S) (Fig. 9); and northwest Argentina (Fig. 11), from its border with Bolivia and south, to include the altiplano and an extensive \textit{valliserrana} (highland, intermontane valleys) region as far
as Angualasto (30.01°S), just south of La Rioja. The central Andean highland belt of copper sulfarsenide ores continues from Peru into northern Bolivia (e.g., at the Lauarani mine), northern Chile (at the giant Collahuasi and Chuquicamata mines) (Fig. 9), and northwest Argentina (e.g., at the Capillitas and La Mejicana/Famatina deposits) (Fig. 11). These deposits are smaller, more sporadic, and bear mineral of far lower quality than those in Peru, however. The two open pit, industrial mines at Collahuasi and Chuquicamata in northern Chile, though vast in size, exhibit highly disseminated, porphyritic copper ores that require the processing of massive volumes of low grade mineral to produce economically viable yields. Nevertheless, remnants of enargite veins at Chuquicamata were still accessible in 2006 when Lechtman visited the mine and sampled enargite mineral directly from those veins. Prehistoric mining of small bodies of higher grade or supergene enriched ore exploited at Chuquicamata and Collahuasi would almost certainly have exposed ores whose lead isotopic characteristics are identical to those of the bulk of the orebody.

Some occasional and minor production of small arsenic bronze artifacts in northwest Argentina was accomplished at the outset of and during the Middle Horizon (Fester 1962; Ziobrowski et al. 1996) through exploitation of arsenic-bearing copper ores such as those at the Capillitas mine near the Hualfín Valley (Fig. 11) (Fester 1962; A.R. González 1979; L. R. González 2004). What propelled northwest Argentina to initiate a much larger-scale production of tin bronze must have been access to supplies of tin (cassiterite ore) during the Regional Integration or Middle Period (CE 400-900). Later, during the Regional Development Period (CE 900-1400), tin bronze discs, some weighing as much as 30 kg, ceremonial axes, and large bells became central to the expression of religious ideology in northwest Argentina and were items of high social status (L. R. González 2004).
The extensive and rich cassiterite [SnO$_2$] ore field that runs from the southwestern shores of Lake Titicaca south through the Bolivian altiplano and into northwest Argentina is unique not only to the Andes but to all of South America. It is one of the richest cassiterite fields in the world (Lechtman 2003b, fig. 3).

Tin bronze figured prominently at Tiwanaku, the large, Middle Horizon pilgrimage center and perhaps political capital, located near the south shores of Lake Titicaca, on the Bolivian altiplano (see Fig. 13). Tin bronze was also an important alloy at sites such as San Pedro de Atacama, in Chile (see Fig. 13), that were well within Tiwanaku’s sphere of influence. There is no consensus about the origin of tin bronze metallurgy in the south-central Andes, whether the technology moved from northwest Argentina north to Tiwanaku or from Tiwanaku south (A. R. González 1992; L. R. González 2004; Lechtman 2014). The richest portion of the cassiterite field lies in what is today Bolivia, the mineral becoming more dispersed as the field reaches south. Nevertheless, in northwest Argentina lost wax casting was practiced commonly in the production of tin bronze items of a size and complexity that are rare in the Titicaca basin. Within the Tiwanaku sphere, tin bronze alloy was cast often into rod-like ingots which were shaped subsequently into artifacts through extensive plastic deformation of the solid metal. There is scant evidence of lost wax techniques having been used at Tiwanaku.

The most interesting, rare, and unexpected of Middle Horizon bronze alloys is the ternary alloy of copper, arsenic, and nickel (Cu-As-Ni) that appears first at Lukurmata/Tiwanku at the onset of the Middle Horizon (ca. CE 250-500) (Lechtman 2003a). The ternary bronze predates tin bronze in the Lake Titicaca basin. Both bronze types were used concurrently for the same range of objects – primarily small tools and personal adornments -- but the ternary bronze was favored for the production of architectural cramps used in the massive stone, monumental
constructions of the Akapana and Pumapunku temples at the capital (Lechtman 1998). From its first appearance until later in the Tiwanaku sequence (roughly CE 500-800), the ternary alloy dominated the bronze inventory, capturing 82% of all Tiwanaku bronze artifacts that have been analyzed from this period (Lechtman 2003a). During the apogee of Tiwanaku influence in the south-central Andes (CE 800-1000), the ternary bronze alloy continued to dominate the bronze corpus at Tiwanaku: 55% of items analyzed were made from the ternary alloy, 27% were made from tin bronze (a few items were of copper or arsenic bronze). Only during the final phase and decline of Tiwanaku was the ternary alloy abandoned in favor of the binary tin bronze (83% Cu-Sn:17% Cu-As-Ni) (Lechtman 2003a). At San Pedro de Atacama, also, the Cu-As-Ni alloy was a primary component of the bronze inventory during the Middle Horizon (Lechtman and Macfarlane 2005, 2006). During the field surveys we attempted to sample ore deposits with reported mineralization in nickel or nickel arsenide (NiAs, nickeline), but we have been unsuccessful so far in determining the mineral source that provided nickel to this bronze alloy.

Towards the close of the Middle Horizon the copper-tin alloy emerged as the bronze preferred both in the Titicaca basin and in northwest Argentina. Centuries later, the Inka chose tin bronze as the alloy of state, disseminating it throughout Tawantinsuyu, their empire, as far north as Ecuador, where it was incorporated as an exotic material (Lechtman 2007). Tin bronze is the alloy we associate most often with the imperial Andean Late Horizon.

**Tiwanaku and its ‘Metallurgical Reach’**

**Tiwanaku and San Pedro de Atacama**

Investigators who study the emergence of a Tiwanaku state during the Middle Horizon examine the role of south-central Andean altiplano populations in the development of Tiwanaku and the reciprocal role Tiwanaku played in the emergence of complex societies in the
circumpuna region. At the southernmost limits of Bolivia, the Lípez province that borders on northwest Argentina (see Fig. 9), Nielsen (1997, 1998, 2001, 2002, 2006) has explored the function of agropastoral communities in the development of long distance, interregional exchange networks such as those that were active and central to the relationships between San Pedro de Atacama and Tiwanaku during the Middle Horizon.

San Pedro de Atacama, a high (2414 masl, on average) oasis in the north Chilean Atacama desert, served as an entrepôt through which sumptuary goods were distributed from Tiwanaku to other regions, especially to the south (Berenguer et al. 1980; Kolata 1993; Llagostera 1996), and San Pedro sent to Tiwanaku non-local materials, either native or processed -- perhaps including bronze alloys -- that came from regions as distant as northwest Argentina (Núñez 1987; Núñez and Dillehay 1979). These goods were transported by llama caravans. A significant section of the southern route that ran north crossed the altiplano through the Lípez (Berenguer 2000), ultimately reaching San Pedro to connect the oasis with Tiwanaku (Fig. 9).

Along much of this journey the llama caravans passed through zones rich in ores of copper, arsenic, and tin. Núñez (1987) maintains that these caravans, organized by herders who were also miners, were responsible for transporting metal and metal objects along great north-south distances, between coast and sierra, and that these herdsmen-miners travelled commonly to exploit ores at locations far from their centers of ethnic affiliation.

One of the most carefully studied of the south-central Andean exchange networks developed in conjunction with mining and metallurgical activities within the Chuquicamata mining district (Fig. 9) of northern Chile (Núñez et al. 2003) during the Middle Horizon and into the Late Intermediate Period (ca CE 780-1020). Chuquicamata is today one of the world’s largest, industrial, open pit mines exploited for its porphyry copper ore deposits. In prehistory,
miners accessed rich veins of atacamite $[\text{Cu}_2\text{Cl(OH)}_3]$ ore, both exposed (Núñez et al. 2003) and at shallow, subsurface levels (Bird 1979), that was crushed and later smelted to copper ingots (Núñez et al. 2003). Núñez and his colleagues (2003) argue that between about CE 400 and 900 – from the early Middle Horizon to the greatest extension of Tiwanaku’s presence in the south-central Andes – mining camps at Chuquicamata were occupied by miners-caravan drovers from the San Pedro de Atacama oasis and from the Loa River basin. The line-of-flight distance between San Pedro and Chuquicamata is approximately 95 km (Fig. 9). Somewhat later, during the Late Intermediate Period (ca CE 1020-1400), these mining colonies formed close relationships with caravan groups whose networks extended into the upper reaches of the Loa River and the adjoining altiplano (Núñez et al. 2003).

**Tiwanaku and San Pedro de Atacama: a lead isotope investigation of ternary Cu-As-Ni bronzes**

It has been suggested that San Pedro de Atacama transshipped metal, probably in the form of ingots, to Tiwanaku through its active network of llama caravans. The further implication of this argument is that the ore source for the metal may likely have been Chuquicamata (Núñez 1987).

A large proportion of Middle Horizon bronze artifacts excavated at Tiwanaku and at San Pedro de Atacama is made from the ternary Cu-As-Ni bronze (Lechtman 2003a; Lechtman and Macfarlane 2005, 2006). Lechtman’s (2003a) analyses of a group of 31 assorted metal artifacts from Tiwanaku and Lukurmata demonstrate that, between Late Formative 2 and Late Tiwanaku IV (ca. CE 300-600) (Janusek 2008: fig. 1.7), 82% of copper-base objects excavated from these sites are ternary bronzes; only nine percent of the artifacts are made from Cu-As alloys, and another nine percent from low-tin, Cu-Sn alloys. Between Late Tiwanaku IV and Early Tiwanaku V (ca CE 600-800), this situation changed dramatically when almost one-third of all
Tiwanaku objects were made from tin bronze, though the majority (55%) continued to be fashioned from the ternary bronze alloy.

At San Pedro de Atacama, Lechtman analysed 80% of the axes [N=36] in the collection of the Museo Arqueológico Gustavo Le Paige (Lechtman and Macfarlane 2005). Twenty-two of these (61%) are made of the ternary Cu-As-Ni alloy. Whereas the reliability of chronological control of the San Pedro corpus is not comparable to that of the more recently excavated material at Tiwanaku, nevertheless many of the San Pedro axes have been identified as clearly of Middle Horizon origin (Lechtman and Macfarlane 2005).

Figure 14 presents a plot of the lead isotope ratios this study determined for a group of copper ore deposits and mines in the vicinity of Tiwanaku. The locations of the Don Carlos and extensive Corocoro mines can be found on the maps in Figures 6 and 7. Except for one or two outliers, all the lead isotope signatures for these ore deposits and mines fall within the field of province IIIa.

Figure 15 plots the lead isotope signatures we determined for 14 Cu-As-Ni Middle Horizon bronzes from Tiwanaku. Without doubt, nine of these lead isotope artifact analyses fall within province IIIa, and the remaining five plot within province IIIb. Figure 15 also delimits the range of lead isotope compositions determined for the ores close to Tiwanaku that are presented in Figure 14. These ore and artifact isotope data demonstrate that the majority of the Tiwanaku ternary bronze artifacts analyzed were made from ores that were obtained locally.

The five remaining artifact isotope signatures in Figure 15 fall into province IIIb. As the ore deposit site maps in Figures 6 and 7 indicate, there are two locations in the south-central Andean region that host ore bodies whose lead isotope signatures fall in province IIIb: (1) the cluster of ores at Sarita, Condoriqueña, and Martha, just north of and slightly west of Lake
Titicaca in the Carabaya zone of highland, southeast Peru – the location of the Inka and pre-Inka Chuquiabo gold mines (Berthelot 1986); and (2) the cluster of ores at Huancané, Lipiña-Galan, and Toldos in the southern Lípez of Bolivia. We cannot determine which of these two province IIIb regions was the source of ores that provided metal for the five Tiwanaku artifacts. The relative closeness of San Pedro to the southern Lípez, high sierra ore sites (see Figure 6) may lend some weight to an argument for use of a Bolivian ore source(s). Table 3 presents the lead isotope ratios determined for the Cu-As-Ni bronze artifacts from Tiwanaku.

As the isotope plot in Figure 15 demonstrates clearly, none of the Tiwanaku ternary bronze artifacts was made from ores whose isotope signatures fall into either province I, e.g., ores from Chuquicamata or Collahuasi, or province II, e.g., the ore deposit at Chulacao, just south and east of San Pedro.

Figure 16 presents a plot of the lead isotope signatures this study determined for 16 Middle Horizon axes from San Pedro de Atacama. Of these, 12 exhibit lead isotope ratios that derive unequivocally from ore deposits in provinces IIIa, IIIb, or IV. Among the axes whose isotope signatures derive from altiplano sources, half lie in or are close to the province IIIa field, and they fall within the zone of analyses determined for ores located close to Tiwanaku.

Four of the San Pedro axes exhibit lead isotope signatures that fall into province IIIb. Two of the axes show much lower values of $^{206}\text{Pb}/^{204}\text{Pb}$ than any of the others. These axes may have been made from ores whose lead isotope signatures are typical of province IV, which occupies the Bolivian Lípez and altiplano zones of western Bolivia. Of the remaining three San Pedro axes, all exhibit lead isotope signatures consistent with ores derived from the Chulacao mine (province II), and two of the three have lead isotope ratios consistent with province I mines.
such as those at Chuquicamata and Collahuasi. Table 3 presents the lead isotope ratios determined for the Cu-As-Ni bronze axes from San Pedro de Atacama.

The Tiwanaku and San Pedro de Atacama lead isotope study of Middle Horizon ternary bronze alloy artifacts demonstrates conclusively that most of these artifacts that were excavated at Tiwanaku were made from ores located in the general vicinity of the site. None of these artifacts was made from ores derived from isotope province I, the orogene, coastal batholith-emplaced ores. A similar picture presents for the ternary bronzes from San Pedro. They, too, were made primarily from high sierra and altiplano ores, although the San Pedro artifacts exhibit a broader range of ore source types.

The study points to the utility of lead isotope analyses determined for ores and artifacts in the south-central Andes in discriminating between major ecological zones, in this case between the altiplano and high sierra on one hand and the coast and lower western Andean mountain slopes (jungas) on the other. The results indicate the likelihood that in some cases Tiwanaku’s reach for copper-based metallic ores was as distant as the southern Lípez of Bolivia, where we know from the studies of Nielsen (1997, 2006) and others (Núñez and Dillehay 1979; West 1981; Lecoq 1985, 1987, 1999; Merlino, Sánchez, and Ozcoidi 1988) that an active exchange network of llama drovers carried goods, perhaps metallic ores, from as far south as northwest Argentina and moved them north, ultimately to the capital at Tiwanaku.

Given the lead isotope results reported in Figures 14, 15, and 16, we can argue with a high degree of confidence that the sources of metal used at Tiwanaku to fashion the Cu-As-Ni bronze artifacts that dominated the bronze inventory there during the early and middle phases of the Middle Horizon were ores exploited on the altiplano, at sites often not far from Tiwanaku itself. The altiplano was also the primary source of ores for the Cu-As-Ni bronze alloys used to
produce the axes excavated at San Pedro de Atacama. We do not have archaeological evidence at this time that locates extractive metallurgy sites (smelting sites) that provided the ternary bronze alloys to either Tiwanaku or to San Pedro. The likelihood is high, however, that such sites are in the Bolivian altiplano or high sierra, such as the Lípez PULAC 050 smelting site (Lechtman et al. 2010) discussed in the following section.

Whereas these lead isotope investigations help clarify the sources of copper ores or arsenical copper ores that were smelted to produce Cu-As-Ni bronzes, they do not allow us to determine the source(s) of nickel in these ternary alloys. The presence of nickel in high concentration in Middle Horizon copper-arsenic bronze alloys (Lechtman 2003a; Lechtman and Macfarlane 2005) is remarkable, because nickel minerals occur rarely anywhere in the Andean region. We discuss the presence and presentation of nickel mineralization in the central and south-central Andean zone (Lechtman 2003a; Lechtman and Macfarlane 2005, 2006) and point out that the sources of nickel, while scarce, need not necessarily have been proximate to either Tiwanaku or San Pedro. The wide range of province III lead isotope values determined for the San Pedro axes suggests that the lead in those alloys came from many province III, isotopically different copper ores rather than from a small number of nickel deposits (Lechtman and Macfarlane 2006). Apparently the lead isotope values associated with nickel minerals that were smelted together with copper minerals are not sufficiently different to produce a detectable effect in the analyses we have made; or, the concentrations of lead in the ores that contain nickel are much too low to influence the lead isotope compositions of alloys made with province III ores that contain copper (Lechtman and Macfarlane 2006). We suggest that using the isotope ratios of osmium, an element that is present in far greater concentrations than lead in rocks that contain nickel, may prove helpful in identifying the sources of nickel in Middle Horizon ternary bronzes.
For example, osmium isotope ratio analyses should allow us to determine whether the nickel in the ternary alloys came from a source in province I, as distinct from province III (Lechtman and Macfarlane 2006: 518).

**Tiwanaku and Pulacayo**

The town of Pulacayo, an Industrial Heritage site, now an almost abandoned mining camp, is located at 4200 masl on the Bolivian altiplano, 25 km north northeast of Uyuni (Fig. 9), at the southeastern limit of the Salar de Uyuni, the largest salt flat in the world. The rich Pulacayo polymetallic silver-lead-zinc-copper ore deposit, known to have been exploited principally for silver since Spanish colonial times, covers approximately 22,850 hectares centered on the historical Pulacayo mine and town site. The deposit has been mined intermittently since the mid-19th century and was the largest silver mine in Bolivia during the first half of the 20th century. Recent archaeological and metallurgical investigations at PULAC 050, a Middle Horizon extractive metallurgical site located some 10 linear km due south of Pulacayo, indicate that the Pulacayo ore deposit was exploited for copper and likely for silver during the period of Tiwanaku sway on the southern Bolivian altiplano (Cruz 2009; Lechtman et al. 2010).

In 2005 Pablo Cruz (Cruz 2009) initiated an archaeological survey of the high Bolivian puna that focused on the region beyond the eastern and southern limits of the Salar de Uyuni, including Pulacayo. Prior to his study, that region had been considered a human wasteland in prehistory, largely uninhabited and marginal with respect to nuclear centers located on the altiplano surrounding Lake Titicaca and throughout the Bolivian puna. Within his initial 250 km sq. survey area, Cruz located numerous individual and collective burial sites, habitation sites,
llama caravan camps (jaras), several caravan trails, and three sites with clear evidence of metallurgical activities, including the PULAC 050 site.

Under the auspices of the Pulacayo Archaeological Project sponsored by ASUR (Antropólogos del Surandino), in 2006 Cruz and Lechtman began study of the small PULAC 050 site to investigate its technological functions, its possible relationship to the Pulacayo ore deposit located 10 km to the north, and its date within the south-central Andean chronological sequence (Janusek 2008). Assignment of the site to the Middle Horizon would require assessment of the place of PULAC 050 within the larger economic and cultural landscapes defined by the prevalent long distance interaction spheres that lay between Lake Titicaca and the north Chilean oasis at San Pedro de Atacama (Lechtman et al. 2010).

PULAC 050, located at an altitude of 3850 masl, was an extractive metallurgy site where several furnaces of different design were built to smelt metallic ore and probably to refine smelted metal. To date we have defined three distinct sectors at the site: an ore preparation area, an ore smelting and metal refining area, and what appears to have been a workshop area where excavation of one of the walled workshop enclosures revealed stored copper ore and a variety of pumice blocks and polishing tools dispersed on the floors (Lechtman et al. 2010).

The ore preparation area is strewn with green copper mineral (XRD analyses identified tenorite, cuprite, malachite, azurite, atacamite) that had been comminuted with large grinding stones. Both surface and excavated materials from the furnace area include smelted copper metal, copper matte (copper sulfide), lead metal, and metallurgical slags some of which appear to have been products of the first stage of smelting silver-rich ores with associated lead and copper mineral components (Lechtman et al. 2010).
Figure 17 presents a lead isotope plot that locates the isotope signatures of ore mineral from the Pulacayo mine as well as the lead isotope ratios of various items from the PULAC 050 site: green copper mineral, droplets of smelted copper metal, and a piece of copper matte produced during the smelting of sulfur-containing copper ore. Four of the six isotope data points determined for ores collected at the Pulacayo mine form a tight cluster on the lead isotope plot in Figure 17. The lead isotope signatures of PULAC 050 copper mineral, smelted copper metal, and copper furnace matte all fall within the tight cluster presented by the Pulacayo mine ore isotope ratios. We do not hesitate to argue that the copper ores, and probably the silver-rich ores, smelted at PULAC 050 were exploited at the Pulacayo polymetallic ore deposit and brought to the site for extraction. The droplets of smelted copper metal and the copper sulfide matte are all smelting products of Pulacayo deposit ores.

The Pulacayo and PULAC 050 lead isotope signatures have been included on the isotope plot for ores from northwest Argentina (Fig. 12). They appear in Figure 12, because lead isotope values for the Argentine Pan de Azúcar mine cluster close to, and in several cases overlap, the Pulacayo-PULAC 050 isotope array. This is an excellent example of the coincidence of lead isotope ratios of ore bodies that are geographically distant within the same isotopic province. Pan de Azúcar, a pyrite-rich and copper-poor Ag-Pb-Zn deposit currently being reevaluated for gold (Igarzabal 1969), is located approximately 160 line-of-flight km south of the Pulacayo polymetallic ore deposit.

Several AMS (accelerator mass spectrometry) and radiocarbon determinations of materials encountered at the PULAC 050 site indicate that metallurgical activities were in place there during the Middle Horizon and continued through the latter part of the Late Intermediate Period. A charcoal sample excavated from a hearth in one of the walled-in workshop
compounds yielded a two sigma calibrated value of cal CE 563-889 (Middle Horizon) (Lechtman et al. 2010). Three other charcoal samples, excavated within the metallurgical furnace area, were analyzed by AMS and yielded calibrated two sigma dates (Cruz and Lechtman unpublished Beta Analytic radiocarbon laboratory report: 1.x.2012). At an excavated depth of 60 cm below the first occupation level, a sample from within a combustion chamber yielded a value of cal CE 890 (Middle Horizon: this value represents a single intercept of the radiocarbon age with the calibration curve; the two sigma calibrated results include CE 780-790, CE 810-850, and CE 850-980); a second sample from compact sediment at the first occupation level yielded a value of CAL AD 1020-1160 (early Late Intermediate Period); a third sample from an excavated depth of 60 cm, located outside the wall of a combustion structure, yielded a value of CAL AD 1290-1410 (late Late Intermediate Period). These calibrated two sigma radiocarbon dates indicate that metal extraction and refining operations were in process at PULAC 050 during the middle-to-late Middle Horizon. Additional supporting evidence as to the period of occupation and activities at the PULAC 050 site is provided by surface-scattered, decorated ceramic sherds attributable to Puqui, but especially to Yura populations who, during the Middle Horizon, inhabited zones on the eastern flanks of the Salar de Uyuni and to the north of Pulacayo as far as the intermontane valleys of Potosí (Ibarra Grasso 1973; Ibarra Grasso and Lewis 1986; Lecoq and Céspedes 1997a, 1997b; Céspedes and Lecoq 1998; Lecoq 1999; Cruz 2009).

Archaeological interest in the Pulacayo area was stimulated in the mid-1990s when a resident of the region discovered a small funerary cave within a sedimentary outcrop that contained five human burials. Accompanying the burials was a rich assortment of extremely fine prestige items, especially garments (see Fig. 18), many of which exhibit the style, iconography,
and production techniques common to Tiwanaku elite material culture. A radiocarbon
determination of a bone fragment from one of the cave burials yielded a two sigma value of cal
CE 674-874 (Middle Horizon) (Lechtman et al. 2010).

One of the metal artifacts found in the so-called ‘Pulacayo Cave’, illustrated in Figure 19,
is a tin bronze brazal, or arm band, of a variety that has been encountered almost exclusively in
Bolivia, Chile, and northwest Argentina. The bronze alloy contains 9wt% Sn. The result of a
lead isotope analysis of a small sample removed from the brazal is plotted in Figure 17. The
isotope signature of the brazal lies well within the isotopic field determined for the Pulacayo ore
deposit, and it fits close to the tight cluster of isotope signatures for the PULAC 050 copper
mineral, smelted copper metal, and copper sulfide matte. We have no evidence at this time that
would allow us to determine where the Pulacayo cave brazal was manufactured, but the lead
isotope evidence presented in Figure 17 is consistent with the copper metal in the brazal alloy
having been extracted from Pulacayo deposit ores, and those copper ores could have been
smelted at the PULAC 050 site. Table 4 presents lead isotope ratios determined for Pulacayo
ores, PULAC 050 copper mineral, smelted copper metal, and furnace copper sulfide matte, as
well as for a sample removed from the Pulacayo Cave brazal.

Recent studies (e.g., Lechtman, Ed. 2006) of the dynamics governing the movement of
people and goods throughout the western Andean altiplano in prehistory and in the present,
describe centers, or nodes, of economic and cultural development within and proximate to the
zone, such as Tiwanaku and San Pedro de Atacama. Of special and critical importance to these
dynamics are the spatial “internodes” (Nielsen 2006), considered as transit/stopping-over places
or regions for supplying natural resources to the centers. From this perspective, the Pulacayo
zone represents the archetypal internode (Lechtman et al. 2010).
Pablo Cruz’ archaeological investigations proximate to the eastern rim of the Salar de Uyuni demonstrate that during the first and second millennia CE the Pulacayo region was densely populated and achieved levels of social and technological complexity during the Middle Horizon (Cruz 2009; Lechtman et al. 2010). Communities participated actively in the long distance exchange networks for the circulation of prestige objects and objects of high symbolic value that developed within the south-central Andes and that played a significant role in supporting the growth of the Tiwanaku state. We know now that these communities contributed to the supply of basic materials, such as copper and tin bronze, from which many of these highly sought-after objects were made.

The PULAC 050 site was evidently populated, perhaps seasonally, by specialists in the extractive metallurgy of both copper and silver ores. It may represent one in a chain of such sites not recognized previously in the south-central Andes. The variety and sophistication of its smelting furnaces and the centralization of metal production at the site are features of the Middle Horizon (Lechtman et al. 2010). The archaeological and lead isotope studies reported here of the Pulacayo area metallic ores and associated artifacts provide strong evidence for the extent of the ‘metallurgical reach’ of Tiwanaku during the middle to late Middle Horizon.

**Wari**

During the Middle Horizon, the large, urban center at Wari (2600-3000 masl), in the Ayacucho Valley (Fig. 13), was the capital of a vast, expansive state – perhaps an empire – established in the central Andean highlands and along the southern coastal valleys of what is today Peru. The Wari and Tiwanaku ‘spheres of influence’ were largely coeval though geographically and topographically separate (see Fig. 13).
We are just beginning to assemble and to compare data regarding the production of bronze alloys and items of bronze from several Wari highland administrative centers located to the south of the capital: Conchopata, Pikillacta, and Cerro Baúl (Fig. 13). Analyses of alloy composition determined for artifacts excavated at Conchopata (see Table 5), Pikillakta (Lechtman 2005) and at Cerro Baúl (Lechtman 2003b; Dussubieux and Williams 2009) reveal them to be almost exclusively copper-arsenic bronzes. To date, lead isotope analyses have been carried out, and are reported here, only on Wari artifacts excavated at Conchopata.

**Conchopata**

Conchopata, a sizeable urban center located some 10 km to the south and just to the west of Wari (Fig. 13), in the Huamanga Basin at the southern end of the Ayacucho Valley, covered at least 20 ha. Much of the site has been lost to the construction of a regional airfield and other development as the modern city of Ayacucho grew. Radiocarbon determinations indicate that Conchopata was not abandoned with Wari’s rise to supremacy (Isbell and Cook 2002) but remained an important residential center until at least CE 900-1000. The metal artifacts discussed here are best dated within the range of the majority of calibrated radiocarbon dates for Conchopata: ca. CE 700 - 900 (William Isbell, personal communication).

Denise Pozzi-Escot (1991) and William Isbell (2000) contributed 24 metal artifacts to this study from their excavations in Sectors A and B at the site. The data presented here for Conchopata include not only artifact compositions, reported in Table 5, but also artifact lead isotope signatures, given in Table 6. Of the 19 artifacts analyzed for their composition, 16 are made from copper-arsenic alloys, one is made from copper, one is made from a ternary Cu-Ag-As alloy, and one is made from a Cu-Pb alloy. The Conchopata data confirm the compositional type of Wari highland bronzes as arsenic bronze. The artifacts studied include
personal items (tupus exclusively), small tools (hand tools, needle, nail, mace head/bola), and a small assortment of miscellaneous items. The Conchopata artifact inventory resembles closely that excavated at Pikillacta (Lechtman 2005).

Lead isotope ratios determined for 20 artifacts from Conchopata (see Table 6) define a large and distinct array on the $^{208}\text{Pb}/^{204}\text{Pb}$ vs $^{206}\text{Pb}/^{204}\text{Pb}$ diagram (Fig. 20). The size and position of this data array cannot be explained by any single known Andean copper ore source. The lower end of the array plots within the range of province IV ores, and it overlaps with province I ores as well. The upper end of the Conchopata array also overlaps important Peruvian province II ore deposits, including the isotope compositions determined for the large Cerro de Pasco copper deposit, but it also coincides with ore compositions from some smaller, inland province III ore deposits.

The complex, heterogeneous lead isotope signatures of the Conchopata artifacts could indicate that ores from as many as four different isotope provinces (I, II, IIIa, and IV) were involved in their production. Because province II ore lead is defined as a mixture of lead from provinces I and IIIa, the Conchopata artifact lead isotope compositions could more simply result from a combination of ores from province II with ores from province IV.

A still simpler explanation, however, may lie in the lead isotope signatures of ores from Julcani, a copper-bearing, arsenical polymetallic deposit (Petersen et al. 1977) located approximately 68 line-of-flight km northwest of the Conchopata site (Fig. 13). The Julcani ore deposit (4200 masl) exhibits a marked zoning sequence in the form of veins of metallic minerals. Hydrothermal systems deposited broad zones of enargite-pyrite-tennantite/tetrahedrite minerals: enargite and tennantite are copper sulfarsenides; tetrahedrite is a sulfosalt of copper and antimony.
Ore samples from Julcani, originally classified by Macfarlane et al. (1990) as part of province II, have an anomalously broad range of lead isotope ratios, reflecting unusually diverse sources of ore lead. Julcani has by far the largest lead isotope variability yet documented for an arsenical copper-bearing ore deposit in the Andean zone. The upper end of the Julcani data defines a clear province II array and overlaps substantially with the Conchopata samples (Fig. 20), whereas the lower end extends to $^{206}\text{Pb}/^{204}\text{Pb} < 18$, indicating a province IV component. Porphyry copper deposits in province IV in southern Peru such as Toquepala show mixing toward the low $^{206}\text{Pb}/^{204}\text{Pb}$ component, but do not have the province II component.

Although the presence of Julcani fairly near the Conchopata site does not rule out the other possible models of ore mixing, it does suggest a simpler and persuasive explanation for the compositions of the Conchopata artifacts.

The lead isotope signatures for the 14 artifacts analyzed from Tiwanaku (Fig. 15) are included in the lead isotope plot for Conchopata (Fig. 20) to demonstrate: (1) that the Conchopata array is distinct and completely different from the Tiwanaku array, and (2) that the Bolivian altiplano ores that provided the source material for producing the large majority of Middle Horizon ternary Cu-As-Ni bronze artifacts in the south-central Andes did not serve as source material for the production of Cu-As bronzes in the central Andean highlands.

**Pikillacta and Cerro Baúl**

Pikillacta, one of the largest and best preserved Wari provincial centers (3250 masl), is located in the Lucre Basin at the eastern end of the valley of Cusco (Fig. 13). Radiocarbon and Accelerated Mass Spectrometry (AMS) carbon analyses have determined that the center was occupied from about CE 600 to its abandonment between CE 900 and 1000 (Gordon McEwan,
personal communication; Glowacki 2005). Pikillacta is the southernmost Wari administrative center in the central Andean highlands.

The group of 30 metal artifacts from Pikillacta that have been analyzed for composition, predominantly tupus, also includes needles, pins, spoons and spatulas (Lechtman 2005). Of the 30, 26 are arsenic bronzes, and one is made from the Cu-As-Ni ternary bronze alloy (Table 7).

Cerro Baúl, an important, fortified, but much smaller Wari civic-ceremonial center in the lower Moquegua River valley (2600 masl) on the far south coast of Peru (Fig. 13), was an intrusive Wari political colony or outpost situated well within Tiwanaku territory. Similar to the Pikillacta metal artifact corpus, the Cerro Baúl metal inventory is dominated by tupus and tupu fragments (Lechtman 2003b).

Of the 31 metal artifacts analyzed from Cerro Baúl (Lechtman 2003b; Dubussieux and Williams 2009), 20 are arsenic bronzes, two are made from the ternary Cu-As-Ni bronze, and two are apparently made from the ternary bronze alloy to which tin was added (Cu-As-Ni-Sn), producing a quaternary bronze alloy. Three of the Cerro Baúl artifacts are made from tin bronze (Table 7). Whereas Cerro Baúl is situated far to the south of Pikillacta, within Tiwanaku territory, nevertheless a majority ($\approx 65\%$) of the Baúl metal corpus is made from arsenic bronzes.

Both Lechtman (2003b) and Dussubieux and Williams (2009) suggest that the Cerro Baúl metal artifacts made from the ternary Cu-As-Ni alloy, presumably a Tiwanaku or at least a south-central Andean bronze alloy, were items imported to Cerro Baúl. Lechtman (2005) suggests further that the two Baúl ternary bronze artifacts came from Cerro Baúl’s near neighbor, Omo, a small Tiwanaku colony situated 10 km south of Cerro Baúl on the Moquegua River drainage (Fig. 13). Almost certainly the two quaternary (Cu-As-Ni-Sn) bronze alloys must derive from the south-central Andean zone and were likely supplied to Cerro Baúl by Omo. The Omo corpus
of 4 metal artifacts analyzed for their composition (Lechtman 2003b) (Table 7) includes a tupu fragment (ternary Cu-As-Ni bronze), a knife fragment (Cu-As bronze), another knife fragment (ternary Cu-As-Ni bronze), and a chisel fragment (Cu-Sn bronze, with minor amounts of As and Ni). The Omo knife fragments are stylistically Tiwanaku. Although the corpus of Omo artifacts analyzed for chemical composition is small, nevertheless all three bronze types are represented: arsenic bronze, the ternary bronze alloy, and tin bronze. This suite of bronzes can be considered typical for a Tiwanaku colony located in a geographic domain occupied by outliers from both Tiwanaku and Wari spheres (see Fig. 13).

Ternary bronze in the Wari sphere: A problem for lead isotope investigation

The Department of Arequipa is located adjacent to and immediately north of the Department of Moquegua in the southernmost regions of Peru. Archaeologists reconsider and remap the zone of contiguity recognized as having existed between the Wari and Tiwanaku spheres of influence during the Middle Horizon in accordance with access to new archaeological data for that zone which, heretofore, has been sparse. Figure 13 locates the Wari-Tiwanaku ‘overlap’ zone as lying roughly between the Camaná-Majes River valley near the southern limit of Arequipa and the Moquegua River valley at the northern limit of Moquegua (Isbell 2006: fig. 2.1).

Ongoing investigations of central Andean Middle Horizon sites located along major river valleys in the Department of Arequipa are furnishing clear evidence in the form of ceramic, cloth, and metal artifacts that demonstrates the impact of Wari influence on the material culture of populations in this region. Jennings (2010, 2012, in press) notes that there is scarce evidence of Wari imperial presence in Arequipa. For the most part, objects that bear Wari iconographic motifs or that appear Wari in form and style were produced locally or in surrounding regions.
The Wari style and ideas associated with Wari spread through interregional exchange without appreciable contact between individual valley sites and the Wari heartland. Neither Wari nor its highland administrative centers were exporting elite goods to the southern Arequipa valleys.

Two Arequipa sites in particular, La Real (589 masl) in the lower, coastal plain of the Majes River valley (Fig. 13) and Tenahaha (2650 masl) in the highland Cotahuasi valley of the Ocoña-Cotahuasi River drainage (Fig. 13), are of special interest to the study reported here. Figure 13 locates La Real as within the Wari-Tiwanaku overlap zone, but Tenahaha lies deeper within Wari territory. Nevertheless, both sites are considered as culturally within the Wari sphere (Jennings 2010, 2012).

Artifacts made of the ternary Cu-As-Ni bronze alloy are present at both sites (Table 7). Velarde and Mora (in Velarde, Mora and Jennings 2012) describe having examined 92 copper, silver, and copper alloy items from the La Real excavations. These include tupus, needles, a spoon, discs of sheet metal, and textile ornaments. Of 10 artifacts (8 tupus, a needle, and a disc) the authors analyzed for chemical composition, the needle and disc were determined to be made from the ternary Cu-As-Ni bronze; one tupu is fashioned from copper, and the remaining seven tupus from arsenic bronze (Table 7).

From Tenahaha, Velarde and Mora (in press) examined 28 artifacts recovered from excavations at the site. One is made from a gold-silver alloy, another from a silver-copper alloy. Twenty-four of the 28 items are tupus. The authors analyzed 11 of these for chemical composition. All 11 tupus are made from the ternary Cu-As-Ni bronze alloy (Table 7). Velarde and Mora (in press) characterize the Tenahaha tupus as looking like Wari tupus but made from what heretofore we have considered a south-central Andean alloy, associated with Tiwanaku and San Pedro de Atacama. These tupus were not supplied to Tenahaha by the capital at Wari or by
Wari’s neighboring, large, urban center at Conchopata. Table 6 demonstrates that 84% of all Conchopata metal artifacts analyzed to date are made of arsenic bronze. None is made of the ternary bronze alloy (see Table 7).

These new data from Arequipa prompt a series of questions concerning: (1) mechanisms for and extent of the geographic distribution of Middle Horizon ternary bronze artifacts and/or the bronze itself, likely in the form of ingots; (2) the ore sources exploited and processed to furnish Arequipa with ternary bronze alloy artifacts; and (3) the sites of production of the bronze alloy and of the artifacts.

From the Preceramic Period (ca. 9400 BP) to the Middle Horizon, two obsidian deposits – at Chivay and at Alca (Fig. 13) – quarried within the southern Peruvian zone that today delimits the Department of Arequipa, provided most of the obsidian used by Andean societies in southern Peru and on the circum-Titicaca northern altiplano (Burger et al. 2000). Long before the Middle Horizon, the quarry at Chivay (4500-4900 masl), in the Colca (Camaná-Majes) River valley, served as the main and special source of obsidian for altiplano inhabitants of the north Titicaca Basin. Chivay continued to be exploited seriously by Tiwanaku during the Middle Horizon in spite of the quarry’s location well within Wari territory (Fig. 13), the construction of Wari-style agricultural terraces near Chivay, and establishment of a Wari administrative center downstream of the obsidian quarry (Burger et al. 1998; Burger et al. 2000; 2006).

Burger et al. (1998; 2000) describe the well-trafficked route followed by altiplano obsidian miners during the Middle Horizon from the obsidian quarry at Chivay to their highland settlements along the western and southern shores of Lake Titicaca. These are ‘natural routes’ that lead upvalley from Chivay to the headwaters of the Colca River, and from there continue across the puna, north as far as Ayaviri and east towards Juliaca (Burger et al. 1998: 210). We
might consider that during the Middle Horizon, ternary bronze in some form was distributed along these same routes, brought from the Tiwanaku region along the altiplano-puna route and down the Colca River to the Chivay area. Alternatively, the bronze artifacts/ingots may have moved north, from the altiplano and through the puna, descending the headwaters of the Ocoña River as far as Alca and Tenahaha in the Cotahuasi River valley (Fig. 13). During the Early Intermediate Period, just prior to the Middle Horizon, this was a favored route along which Alca obsidian was distributed (Burger et al. 2000: fig. 9).

Ternary bronze in the form of alloy or artifacts likely moved readily between river valleys and sites in Arequipa, such as La Real (Majes) and Tenahaha (Cotahuasi). Glascock’s (2012) x-ray fluorescence analyses of 7 Middle Horizon obsidian specimens from La Real identified three early Middle Horizon obsidians there as from the Chivay source (1), the Quispisisa source (1), and the Alca-1 source (1). The four late Middle Horizon obsidians from La Real were all from the Alca-1 source (Glascock 2012; Jennings in press), reflecting the greatly increased exploitation and distribution of Alca obsidian at that time (Burger et al. 2000; Jennings in press). Whatever the intervalley routes for distribution of obsidian and movement of other resources and Wari-style luxury goods (including ceramics, Spondylus shell, blue- and greenstone, fine textiles, feathers, bronze), the routes were frequently and well used during the Middle Horizon (Isbell 2010).

Given the lead isotope analytical results reported here for south-central Andean copper ore bodies (Figs. 10, 12, 14) and for south-central Middle Horizon artifacts made from ternary bronze alloys (Figs. 15 and 16), we can do far better than guess at the likely sources of the ores that were processed to deliver Cu-As-Ni ternary bronze objects to communities in Arequipa. We need only carry out lead isotope studies of samples removed from Arequipa ternary bronze
artifacts at sites such as La Real and Tenahaha to determine if those artifact alloys were produced with south-central Andean ores.

If the lead isotope values for ternary bronze artifacts from Arequipa and those for Tiwanaku/San Pedro occupy separate and distinct isotope fields, then we are constrained to seek the ore source(s) that produced metal for the Arequipa alloys. If the Arequipa and Tiwanaku/San Pedro artifact isotope values are coincident, several questions remain. Where were the Arequipa ternary bronze artifacts produced, and by what mechanisms may either the artifacts or alloy ingots have moved across the divide and deep into the Wari sphere? Was the ‘bronze divide’ breached (Velarde and Mora in press) and, if so, when, for how long, under what impetus, and to what geographic extent?

**Discussion**

The approach detailed in this work may be useful anywhere lead isotope ratios of potential ore sources are documented to have systematic regional variability. The most direct analog to the Andean setting would be another convergent plate boundary setting. In the Andes, volcanic activity and associated ore formation have been related to convergence between the Nazca seafloor plate and the overriding South American plate. Western North America also formed a convergent boundary with the Pacific seafloor until about 30 million years ago. Convergent boundaries may form between two seafloor plates, also producing volcanism and ores, such as in the Philippines and the Japanese islands. Convergent boundaries can also produce collisions between continental masses, which are too buoyant to be subducted into the trench. Such collisions result in large scale deformation of both continental margins where they meet and generally fuse into a new, larger continent. Such a process formed the Appalachian and Ural mountain ranges and is currently ongoing in the Himalayas.
At any convergent boundary, one would generally expect variations in ore lead isotope ratios with distance from the trench, because it is well documented that the chemistry and source materials of convergent boundary magmas typically vary with distance from the trench. Classic studies of this phenomenon have been published on the Japanese islands, related to convergence between the Pacific seafloor plate and Eurasia (Miashiro 1972), and on southern California and Baja California, related to subduction between the former Farallon seafloor plate and North America (Gromet and Silver 1987). Because most metallic ores in convergent boundary settings form as by-products of magmatic activity, it would not be surprising to find systematic ore lead isotope variations in other convergent margin settings.

Similar, large isotopic variations have been documented in the North American Cordillera related to the age of the underlying continental crust and distance from the former convergent boundary (e.g., Farmer and DePaolo 1997). In this case, the geology is somewhat more complex than that of the South American margin, and this affects the lead isotopic variability of ores. For example, in geologically young ore deposits (less than 65 Ma) from southern Mexico there is a clear trend toward higher $^{206}\text{Pb}/^{204}\text{Pb}$ with distance from the trench, but these ores are geographically superimposed on older ore deposits (more than 65 Ma) which do not show an increase of higher $^{206}\text{Pb}/^{204}\text{Pb}$ with distance from the trench (Hosler and Macfarlane 1996; Potra et al. 2013; Potra and Macfarlane 2013), making the archaeological application of the lead isotope method problematic.

The distribution of lead isotope provinces in the central Andes of Peru differs in some key respects from that within our study area. Like the study area, province I is present along much of the Peruvian coast; however, in southern Peru, province IV extends from the highlands down to the coast and interrupts province I. Lead isotope ratios of ores from the far southern
coast of Peru, including those from the Cerro Verde and Toquepala mines, have the low
$^{206}\text{Pb}/^{204}\text{Pb}$ values diagnostic of province IV. This places sources of low $^{206}\text{Pb}/^{204}\text{Pb}$ copper ores within the Peruvian coastal zone, whereas there are no such ores in province I in Chile. In addition, the thick sequence of Paleozoic sediments that occurs in Bolivia and NW Argentina thins dramatically in Peru, so that province IIIa is much less prominent. Instead of province I transitioning away from the trench into province IIIa or IV, in Peru province I transitions into province II, which occupies the high cordillera and includes major polymetallic mining districts such as Cerro de Pasco, Morococha and Casapalca. There is only a handful of known province IIIa deposits on the east side of the Peruvian high cordillera. Because province II ores are defined by the steep arrays they form on lead isotope plots, in Peru larger numbers of analyses are needed to identify which deposits are province II and what their ranges of variation may be.

Finally, although province I ores in Peru are isotopically very similar to those in Chile, they are less homogeneous in $^{206}\text{Pb}/^{204}\text{Pb}$. Lead isotope ratios within the coastal zone of Peru become steadily more radiogenic into northern Peru and Ecuador, forming a shallowly-sloping isotopic array on $^{208}\text{Pb}/^{204}\text{Pb}$ vs. $^{206}\text{Pb}/^{204}\text{Pb}$ diagrams that eventually cuts across the radiogenic end of the province IIIa array. The source of this variation is not well understood at the present time but would present a problem in interpreting any artifacts with compositions lying in the area of overlap.

The basic method outlined in this work is not limited to modern convergent boundaries, or even to convergent boundaries at all. It is important only that there be a coherent geographic pattern in the lead isotopic compositions of ore sources and that that pattern be sufficiently well documented to be useful. Lead isotopic patterns that develop in ore deposits formed within convergent boundaries persist after the boundary becomes inactive, thus extinct convergent...
boundaries or regions where convergence has produced continental collisions, such as the Ural Mountains, would be places to explore. Regions such as continental interiors where very large contrasts in the ages of potential ore sources exist, age differences much larger than those exhibited by Andean ores, present the opportunity to compare ore sources having much larger isotopic contrast.

**Conclusions**

Lead isotope ratio analyses of 174 ore samples from 39 copper-bearing deposits in the south-central Andes add to the existing, published ore lead database of the region, clarifying significantly the distribution there of ore lead isotope provinces. The process of subduction of the Nazca seafloor tectonic plate under the South American continental plate has formed a narrow and deep trench, the Peru-Chile trench, that follows closely along the Pacific coastlines of Peru and Chile. The lead isotope provinces determined for the south-central Andean region are elongated geographically in the N-S direction, roughly parallel to the trend of the Andean cordilleras. This means that ore lead isotope ratios vary strongly from west to east, as a function of their distance from the trench, but they exhibit much less variation from south to north. Within a given lead isotope province, ores located at roughly the same distance east of the trench may have similar or identical lead isotope signatures, regardless of their relative distance apart in a N-S orientation. Consequently, in the south-central Andean zone, lead isotope signatures of ore bodies can be highly useful in distinguishing among the altitudinal ecozones in which they are emplaced: coast, low western sierra slopes, high sierra, puna/altiplano.

The definition of ore lead isotope provinces in the central Andes allows use of lead isotope ratios of archaeological artifacts to constrain the geological sources of the artifacts, provided proper attention is paid to the limitations and ambiguities in the geological data set.
This study concentrated on identifying the south-central Andean ecozones exploited during the Middle Horizon (roughly CE 600-1000) for copper ores used in the production of ternary copper-arsenic-nickel bronzes, a bronze type used commonly at the sites Tiwanaku (Bolivia: 3840 masl) and San Pedro de Atacama (N. Chile: 2414 masl). A primary aim was to determine the metallurgical “reach” of Tiwanaku; from what distances this large altiplano center accessed copper ore or smelted metal.

We determined the lead isotope signatures of copper ores sampled from the vicinity of Tiwanaku south, through NW Argentina, and from coastal Chilean to altiplano deposits, an area of approximately 250,000 km sq. Superimposed on these ore lead isotope graphs we plotted isotope signatures determined from a group of Cu-As-Ni bronze artifacts excavated at Tiwanaku and from a group of ternary bronze artifacts from San Pedro. The plots indicate clearly that all the Tiwanaku bronzes are made from metal derived from smelting altiplano ores (province IIIa), many of them in the vicinity of Tiwanku but others likely from ore deposits in the Bolivian Lípez area, far to the south. The lead isotope signatures of the San Pedro ternary bronzes plot within the same general altiplano isotope ore field (province IIIa) as the Tiwanaku artifacts. Contrary to suggestions in the literature that San Pedro likely extracted metallic ore from the nearby (ca. 95 km) giant deposit at Chuquicamata and transshipped it or metal smelted from these ores to Tiwanaku, the San Pedro artifact isotope signatures do not coincide with the province I isotopic ore field where the Chuquicamata lead isotope signatures cluster. If ternary bronze artifacts were manufactured at San Pedro, they were made from metal smelted from altiplano ores.

This study includes the lead isotope analysis of a group of arsenic bronze artifacts excavated at Conchopata, a sizeable, central Andean highland center located some 10 km to the south and west of Wari, the large, Middle Horizon, urban center and capital of the Wari state.
The lead isotope data suggest that the ore smelted to produce the arsenic bronze was exploited from the Julcani deposit, a copper-bearing, arsenical polymetallic deposit located approximately 68 line-of-flight km northwest of Conchopata.

By incorporating lead isotope data from both the central and south-central Andes, this research helps identify the range of metal ore sources utilized by each of the two great Andean Middle Horizon political and religious centers -- Wari and Tiwanaku -- in their production of bronze alloys. If interpreted with care, the lead isotope ratios of artifacts produced in the Andean zone in prehistory can be used to indicate potential metal sources, or geographic source regions, or to rule out potential source regions. These capabilities can be powerful when considered together with the archaeological context of the artifacts.
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List of tables

1. New lead isotopic data presented in this study for metallic ore and mineral samples from Bolivia, N. Chile and N.W. Argentina

2. Mineral deposits in the south-central Andean study area, with lead isotope data citations

3. Lead isotope ratios of Cu-As-Ni bronze artifacts from Tiwanaku and San Pedro de Atacama

4. Lead isotope ratios of Pulacayo ore, PULAC 050 mineral, furnace matte, and smelted copper, and the Pulacayo cave artifact

5. Composition of copper and copper alloy artifacts from Conchopata

6. Lead isotope ratios of copper and copper alloy artifacts from Conchopata

7. Copper and bronze alloys determined for artifacts from major Wari sites and sites within the Wari sphere
Figure Captions

**Fig. 1** Model of an Andean-type plate margin, showing the subducting seafloor and resulting generation of magmas and igneous rocks and their emplacement into the overlying continental crust. Most Andean copper ores were formed by processes accompanying the emplacement and solidification of magmas in scenarios like this one (From Tarbuck, Lutgens and Tasa 2014: fig. 2.16A) TARBUCK, EDWARD J.; LUTGENS, FREDERICK K.; TASA, DENNIS G., EARTH: AN INTRODUCTION TO PHYSICAL GEOLOGY, 11th, ©2014. Printed and Electronically reproduced by permission of Pearson Education, Inc., Upper Saddle River, New Jersey

**Fig. 2** Relief map of the Andean zone of South America, from Colombia to slightly south of the city La Rioja (29.26S 66.50W), in northwest Argentina. The Nazca Plate is identified, and the Peru-Chile Trench clearly hugs the continental margin, which is dominated by the Andean cordilleras (From USGS Open-File Report mOF10-1083E: Seismicity of the Earth 1900-2007 – Nazca Plate and South America)

**Fig. 3** Schematic representation of the Doe and Zartman (1979: fig. 2.2) model, showing episodic growth of continental crust by addition of orogene material at convergent boundaries

**Fig. 4** Model curves showing the lead isotopic evolution of the mantle (a), orogene (b), upper continental crust (c) and lower continental crust (d) (From Zartman and Doe 1981: fig. 5a)
**Fig. 5** General lead isotope compositional ranges of the available data on the Andean crust, compared with the model curves from Zartman and Doe (1981: fig. 5a) and modified from Kamenov et al. (2002), with data from Gagnier et al. (1996), Egenhoff and Lucassen (2003), and Loewy et al. (2004). Tick marks on the model curves correspond to 400 million year steps in lead isotope evolution. Upper crustal rocks comprise two groups, labeled “high $^{206}\text{Pb}/^{204}\text{Pb}$ source” and “Paleozoic sedimentary rock source”; both groups have $^{206}\text{Pb}/^{204}\text{Pb}$ higher than 18.2. Lower crustal rocks have $^{206}\text{Pb}/^{204}\text{Pb}$ generally lower than 18.2, reflecting loss of U from the rocks in ancient, high grade metamorphic events. Representative “orogene” rocks from the Peruvian Coastal Batholith define a very small area close to the orogene curve of Zartman and Doe (1981). The dashed box encloses the range of ore compositions presented in subsequent lead isotope ratio plots.

**Fig. 6** Map view of the lead isotope provinces in the central and south-central Andes. Province I ores, including active mines, prospects, and mineral occurrences, are designated with red circles (●), province II deposits with yellow triangles (▲), province IIIa deposits with blue squares (■), province IIIb deposits with green diamonds (♦), and province IV deposits with lavender triangles (▲). Deposits associated with major commercial mines are designated with larger bordered symbols (e.g., △ in province IV). Provinces I, II, IIIa and IV appear to be geographically coherent for the most part; province IIIb occurs in a small area of SW Peru and also sporadically in southern Bolivia and NW Argentina.

**Fig. 7** Map view of the lead isotope provinces in the central and south-central Andes. The provinces are identified with the tones/colors in which they appear on lead isotope ratio plots that represent the isotopic signatures determined for individual ore deposits (e.g., see Figure 8). The ore deposits labeled in Figure 6 appear also on this map.

**Fig. 8** (a) Plots of lead isotope ratio values [$^{208}\text{Pb}/^{204}\text{Pb}$ vs $^{206}\text{Pb}/^{204}\text{Pb}$] and [$^{207}\text{Pb}/^{204}\text{Pb}$ vs $^{206}\text{Pb}/^{204}\text{Pb}$] determined for ores define four lead isotope provinces in the central and south-central Andes; (b) map view that locates the corresponding geographic range and approximate boundaries of each of the four Andean lead isotope provinces. The average crustal lead isotope evolution curve of Stacey and Kramers (1975) is shown for reference.
Fig. 9 Map of the western, altiplano zone of Bolivia, from the southern Lake Titicaca Basin to the Lípez region, which extends roughly from Uyuni south to the border with NW Argentina. This entire zone is rich in metallic ore deposits, many of which were exploited during the Middle Horizon (After Lechtman 2003a: fig. 17.42)

Fig. 10 Lead isotopic compositions of ores located in the southern altiplano and puna. Geographically close and isotopically similar deposits are grouped together to reduce the number of symbols. Ore deposits grouped together as “Lípez Province I” include Cerro Colorado, Inez, Eskapa, Escala, Almacén, San Juan de Irismayu, 25 de Julio, and Puca Mokho. Province IIIb deposits typically exhibit compositions ranging from the area of Province 1 toward higher $^{206}\text{Pb}/^{204}\text{Pb}$ values. All data are taken from Table 1

Fig. 11 Map of NW Argentina, locating the Valliserrana (high, intermontane valleys) region with its dense distribution of archaeological sites. Many of the ore deposits whose lead isotope ratios are plotted in Figure 12 are located in the Valliserrana and the puna to the west: e.g., Pirquitas, Cobres, Capillitas (Hualfín Valley), Famatina (Composite map, after L.R. González 2004:151, 154; Acuto 2008: fig. 42.1)

Fig. 12 Lead isotope ratios of ores from northwest Argentina, compared with samples from the Pulacayo mine and the PULAC 050 archaeological site. NW Argentina ores correspond with the lower, middle and upper ranges of the Province IIIa array, depending on their geological age. Taca-Taca represents a Province IIIb deposit, while Famatina corresponds to Province I. Samples from the PULAC 050 archaeological site plotted here correspond to the range of Pulacayo ore samples (see Figure 17) and not to any known NW Argentina deposit, except for Pan de Azúcar, which is a gold deposit

Fig. 13 Map indicating the approximate extent of the Wari and Tiwanaku spheres of influence in the central and south-central Andean zones during the Middle Horizon. The map locates archaeological sites and two prehistoric obsidian source sites mentioned in the text (after Isbell 2006, fig. 2.1)
**Fig. 14** Lead isotope ratios of ores near Tiwanaku. Ore isotopic signatures are predominantly within the range of Province IIIa

**Fig. 15** Lead isotope ratios of ternary bronze artifacts from Tiwanaku. The artifact isotope signatures overlap principally with ores from provinces IIIa and IIIb. Most lie within the compositional range of ores near Tiwanaku

**Fig. 16** Lead isotope ratios of ternary bronze axes from San Pedro de Atacama. The majority of artifact lead appears derived from Province IIIa sources. The data scatter widely in $^{206}\text{Pb}/^{204}\text{Pb}$, suggesting that artifact lead derives from more than one source of ore lead

**Fig. 17** Lead isotope ratios of copper mineral, copper metal and furnace copper sulfide matte samples from the PULAC 050 site compared with ore samples from the Pulacayo mine and a sample from the Pulacayo Cave artifact (see also Figure 12)

**Fig. 18** Detail of a Middle Horizon, Tiwanaku-style *unku* (man’s shirt) with a representation of the sacrificer figure. This extremely fine unku was one of the items discovered in the Pulacayo Cave (from Berenguer 2000: 87)

**Fig. 19** A tin bronze *brazal* (arm band) found in the Pulacayo Cave (from Lechtman et al. 2010, fig. 2)

**Fig. 20** Lead isotope ratios of artifacts from Conchopata and Tiwanaku, plotted together with data for ores from the Julcani mine and ore lead isotope compositional fields
Range of subsequent Pb isotope plots

Lower crust

Upper crust

Orogene

Mantle

206\(^{\text{Pb}}\)/204\(^{\text{Pb}}\)

Ancient metamorphic “Lower Crust”

Paleozoic sedimentary rock source

High \(\text{^{206}Pb}/\text{^{204}Pb}\)
Source

Province I ores in study area

Range of subsequent Pb isotope plots
$^{208}\text{Pb} / ^{204}\text{Pb} = 23.261$
Stacey-Kramers curve

Compositional range of ores near Tiwanaku

95% uncertainty
San Pedro Axes

Compositional range
of Tiwanaku area ores

Province I

Province IV

Province IIIa

Province IIIb

Province IIIb

Stacey-Kramers curve

250 Ma

500 Ma

95% uncertainty

Chulacao Ores

Chuquicamata and Collahuasi Ores
Province IV
Pulacayo ores
Pulacayo cave artifact
Pulac 050 mineral
Pulac 050 metal
Pulac 050 furnace matte

Province IIIa
Province IIIb

Pulacayo cave artifact
Pulac 050 mineral
Pulac 050 metal
Pulac 050 furnace matte

Stacey-Kramers curve

95% uncertainty

208 Pb/204 Pb vs. 206 Pb/204 Pb
Conchopata artifacts
Tiwanka artifacts
Julcani ores

95% uncertainty
Table 1  New lead isotopic data presented in this study for metallic ore and mineral samples from Bolivia, N. Chile and N.W. Argentina

| Sample No. | District        | Location                  | Material Analyzed | $^{206}\text{Pb}/^{204}\text{Pb}$ | $^{207}\text{Pb}/^{204}\text{Pb}$ | $^{208}\text{Pb}/^{204}\text{Pb}$ |
|------------|-----------------|---------------------------|-------------------|-----------------------------------|-----------------------------------|-----------------------------------|
| MIT 5008   | Don Carlos      | 16° 20' 42" S, 68° 06' 54" W | py                | 18.527                           | 15.676                            | 38.703                            |
| MIT 5010   | Don Carlos      | 16° 20' 42" S, 68° 06' 54" W | py                | 18.437                           | 15.667                            | 38.619                            |
| MIT 5012   | Don Carlos      | 16° 20' 42" S, 68° 06' 54" W | py                | 18.706                           | 15.689                            | 38.962                            |
| MIT 5013   | Don Carlos      | 16° 20' 42" S, 68° 06' 54" W | py                | 18.760                           | 15.713                            | 39.053                            |
| MIT 5014   | Don Carlos      | 16° 20' 42" S, 68° 06' 54" W | py                | 18.683                           | 15.683                            | 38.993                            |
| MIT 5015   | Don Carlos      | 16° 20' 42" S, 68° 06' 54" W | py                | 18.447                           | 15.665                            | 38.603                            |
| MIT 5005   | Quimsa Chata    | 16° 38' 00" S, 68° 39' 30" W | cv                | 18.680                           | 15.654                            | 38.96                             |
| MIT 5085   | Quimsa Chata    | 16° 38' 00" S, 68° 39' 30" W | cv                | 18.631                           | 15.607                            | 38.791                            |
| MIT 5020B  | Corocoro (Copacabana) | 17° 10' 09" S, 68° 27' 04" W | cup + (mal)       | 18.627                           | 15.644                            | 38.779                            |
| MIT 5088   | Corocoro (Copacabana) | 17° 10' 09" S, 68° 27' 04" W | cup + (mal)       | 18.624                           | 15.659                            | 38.817                            |
| MIT 5089   | Corocoro (Copacabana) | 17° 10' 09" S, 68° 27' 04" W | cup + (mal)       | 18.636                           | 15.649                            | 38.800                            |
| MIT 5090B  | Corocoro (Copacabana) | 17° 10' 09" S, 68° 27' 04" W | Cu + mal          | 18.682                           | 15.693                            | 38.930                            |
| MIT 5091   | Corocoro (Copacabana) | 17° 10' 09" S, 68° 27' 04" W | Cu + cup + (mal)  | 18.777                           | 15.743                            | 39.168                            |
| MIT 5093   | Corocoro (Vetillas) | 17° 10' 09" S, 68° 27' 04" W | cup + (mal)       | 18.623                           | 15.668                            | 38.839                            |
| MIT 5094   | Corocoro (Vetillas) | 17° 10' 09" S, 68° 27' 04" W | Cu + cup + (mal)  | 18.615                           | 15.674                            | 38.823                            |
| MIT 5095B  | Corocoro (Vetillas) | 17° 10' 09" S, 68° 27' 04" W | mal               | 18.535                           | 15.666                            | 38.655                            |
| MIT 5096   | Corocoro (Vetillas) | 17° 10' 09" S, 68° 27' 04" W | cup + (mal)       | 18.580                           | 15.644                            | 38.742                            |
| 28M05C     | Azurita         | 18° 04' 18.8" S, 68° 09' 35.3" W | cup + (Cu, mal)   | 18.975                           | 15.682                            | 40.415                            |
| 28M05D     | Azurita         | 18° 04' 18.8" S, 68° 09' 35.3" W | cup + Cu + (mal)  | 18.520                           | 15.602                            | 40.189                            |
| 28M05D     | Azurita         | 18° 04' 18.8" S, 68° 09' 35.3" W | cup + Cu + mal    | 18.921                           | 15.698                            | 40.642                            |
| 29M05A     | Cuprita         | 18° 15' 54" S, 68° 04' 06.7" W | cup + mal         | 18.520                           | 15.649                            | 39.763                            |
| 29M05B     | Cuprita         | 18° 15' 54" S, 68° 04' 06.7" W | cup + mal         | 18.122                           | 15.577                            | 38.137                            |
| 29M05B     | Cuprita         | 18° 15' 54" S, 68° 04' 06.7" W | Cu + (mal)        | 18.607                           | 15.661                            | 39.992                            |
| 29M05F     | Cuprita         | 18° 15' 54" S, 68° 04' 06.7" W | cup + mal + Cu    | 18.636                           | 15.664                            | 39.995                            |
| 29M05G     | Cuprita         | 18° 15' 54" S, 68° 04' 06.7" W | cup + Cu + (mal)  | 18.602                           | 15.635                            | 39.945                            |
| 29M05J     | Cuprita         | 18° 15' 54" S, 68° 04' 06.7" W | Cu + (mal)        | 18.323                           | 15.626                            | 38.706                            |
| Code     | Location                  | Coordinates                  | Marker | Lon   | Lat   | Depth |
|----------|---------------------------|------------------------------|--------|-------|-------|-------|
| 23M05A   | Negrillos                 | $18^\circ 49' 58.2'' S, 68^\circ 37' 12'' W$ | cpy    | 18.116 | 15.623 | 38.423 |
| 23M05B   | Negrillos                 | $18^\circ 49' 58.2'' S, 68^\circ 37' 12'' W$ | gn     | 18.098 | 15.595 | 38.332 |
| 22M05B   | Carangas                  | $18^\circ 56' 31.4'' S, 68^\circ 37' 48.2'' W$ | gn     | 18.127 | 15.622 | 38.426 |
| 20M05B   | Guadalupe                 | $19^\circ 41' 27'' S, 67^\circ 42' 45'' W$ | en     | 18.114 | 15.594 | 38.143 |
| 20M05D   | Guadalupe                 | $19^\circ 41' 27'' S, 67^\circ 42' 45'' W$ | en     | 18.095 | 15.545 | 37.996 |
| 20M05E   | Guadalupe                 | $19^\circ 41' 27'' S, 67^\circ 42' 45'' W$ | en     | 18.121 | 15.600 | 38.138 |
| 20M05F   | Guadalupe                 | $19^\circ 41' 27'' S, 67^\circ 42' 45'' W$ | en     | 18.080 | 15.535 | 38.003 |
| 20M05G   | Guadalupe                 | $19^\circ 41' 27'' S, 67^\circ 42' 45'' W$ | en     | 18.143 | 15.574 | 38.115 |
| 19M05A   | Maria Luisa               | $19^\circ 42' 41.6'' S, 67^\circ 42' 57.7'' W$ | gn     | 18.165 | 15.583 | 38.160 |
| 19M05D   | Maria Luisa               | $19^\circ 42' 41.6'' S, 67^\circ 42' 57.7'' W$ | gn     | 18.052 | 15.596 | 38.133 |
| 19M05E   | Maria Luisa               | $19^\circ 42' 41.6'' S, 67^\circ 42' 57.7'' W$ | gn     | 18.048 | 15.466 | 37.739 |
| 19M05F   | Maria Luisa               | $19^\circ 42' 41.6'' S, 67^\circ 42' 57.7'' W$ | gn     | 18.119 | 15.582 | 38.084 |
| 19M05F   | Maria Luisa               | $19^\circ 42' 41.6'' S, 67^\circ 42' 57.7'' W$ | gn     | 18.138 | 15.601 | 38.199 |
| 16M05A   | Chinchilhuima             | $19^\circ 58' 53.5'' S, 68^\circ 21' 34.2'' W$ | cpy    | 18.480 | 15.605 | 38.487 |
| 16M05A   | Chinchilhuima             | $19^\circ 58' 53.5'' S, 68^\circ 21' 34.2'' W$ | py     | 18.452 | 15.584 | 38.436 |
| 16M05B   | Chinchilhuima             | $19^\circ 58' 53.5'' S, 68^\circ 21' 34.2'' W$ | gn     | 18.481 | 15.629 | 38.544 |
| 16M05F   | Chinchilhuima             | $19^\circ 58' 53.5'' S, 68^\circ 21' 34.2'' W$ | gn     | 18.490 | 15.637 | 38.582 |
| 16M05G   | Chinchilhuima             | $19^\circ 58' 53.5'' S, 68^\circ 21' 34.2'' W$ | gn     | 18.478 | 15.604 | 38.483 |
| 16M05K   | Chinchilhuima             | $19^\circ 58' 53.5'' S, 68^\circ 21' 34.2'' W$ | gn     | 18.478 | 15.616 | 38.514 |
| 18M05A   | Veta Khollu               | $20^\circ 19' 18.2'' S, 67^\circ 55' 40.8'' W$ | cup    | 18.476 | 15.633 | 38.618 |
| 18M05B   | Veta Khollu               | $20^\circ 19' 18.2'' S, 67^\circ 55' 40.8'' W$ | cup    | 18.534 | 15.664 | 38.715 |
| 18M05C   | Veta Khollu               | $20^\circ 19' 18.2'' S, 67^\circ 55' 40.8'' W$ | cup    | 18.574 | 15.716 | 38.874 |
| 98M05B   | Pulacayo                  | $20^\circ 23' S, 66^\circ 42' W$ | gn     | 18.601 | 15.640 | 38.790 |
| 98M05A   | Pulacayo                  | $20^\circ 23' S, 66^\circ 42' W$ | gn     | 18.597 | 15.648 | 38.803 |
| 17M05C   | Cerro Colorado            | $20^\circ 34' 17.2'' S, 67^\circ 59' 28.1'' W$ | cup    | 18.573 | 15.621 | 38.451 |
| 17M05G   | Cerro Colorado            | $20^\circ 34' 17.2'' S, 67^\circ 59' 28.1'' W$ | cup    | 18.619 | 15.631 | 38.475 |
| 17M05H   | Cerro Colorado            | $20^\circ 34' 17.2'' S, 67^\circ 59' 28.1'' W$ | cup    | 19.910 | 15.691 | 38.487 |
| Site Code | Location | Lat/Long | Materials | Cu% | Zn% | Pb% |
|----------|----------|----------|-----------|-----|-----|-----|
| Cobrizos 1 | Cobrizos | 20° 59' 37" S, 67°12' 36" W | cup + mal | 18.339 | 15.628 | 38.507 |
| Cobrizos 3 | Cobrizos | 20° 59' 37" S, 67°12' 36" W | cup + Cu + mal | 18.345 | 15.634 | 38.558 |
| Cobrizos 5 | Cobrizos | 20° 59' 37" S, 67°12' 36" W | Cu + cup | 18.368 | 15.637 | 38.571 |
| Cobrizos 6 | Cobrizos | 20° 59' 37" S, 67°12' 36" W | cup + mal | 18.504 | 15.648 | 38.675 |
| Cobrizos 7 | Cobrizos | 20° 59' 37" S, 67°12' 36" W | Cu + (cup) | 18.281 | 15.549 | 38.245 |
| Cobrizos 8 | Cobrizos | 20° 59' 37" S, 67°12' 36" W | mal | 18.309 | 15.598 | 38.417 |
| Cobrizos 12 | Cobrizos | 20° 59' 37" S, 67°12' 36" W | Cu + (cup + mal) | 18.329 | 15.647 | 38.566 |
| 001M05D | Ines | 21° 03' 08" S, 67° 27' 12.5" W | cup + mal | 18.646 | 15.644 | 38.721 |
| KOH 1 | Koholpani | 21°11' 30" S, 67° 09' 15" W | cup + (mal) | 18.706 | 15.671 | 38.749 |
| KOH 2 | Koholpani | 21°11' 30" S, 67° 09' 15" W | cup | 18.658 | 15.648 | 38.731 |
| KOH 4 | Koholpani | 21°11' 30" S, 67° 09' 15" W | cup + (mal) | 21.099 | 15.784 | 38.870 |
| KOH 6 | Koholpani | 21°11' 30" S, 67° 09' 15" W | cup | 18.678 | 15.674 | 38.769 |
| KOH 7 | Koholpani | 21°11' 30" S, 67° 09' 15" W | cup + Cu + (mal) | 18.989 | 15.678 | 38.835 |
| KOH 9 | Koholpani | 21°11' 30" S, 67° 09' 15" W | cup + (py + mal) | 18.646 | 15.633 | 38.623 |
| 03M05A | Eskapa | 21° 13' 49" S, 67° 41' 56.2" W | cup | 18.678 | 15.644 | 38.670 |
| 03M05D | Eskapa | 21° 13' 49" S, 67° 41' 56.2" W | cup + mal | 18.713 | 15.673 | 38.713 |
| 03M05E | Eskapa | 21° 13' 49" S, 67° 41' 56.2" W | cup | 18.645 | 15.629 | 38.574 |
| 03M05J | Eskapa | 21° 13' 49" S, 67° 41' 56.2" W | az | 18.639 | 15.648 | 38.607 |
| 03M05K | Eskapa | 21° 13' 49" S, 67° 41' 56.2" W | cup | 18.764 | 15.667 | 38.691 |
| 15M05J | Huancané | 21° 26' 7.3" S, 66° 32' 19.6" W | cup | 23.261 | 15.908 | 38.560 |
| 06M05A | Puka Mokho | 21° 33' 53" S, 68° 01' 37.7" W | cup | 18.707 | 15.629 | 38.742 |
| 06M05G | Puka Mokho | 21° 33' 53" S, 68° 01' 37.7" W | cup + (Cu) | 18.706 | 15.625 | 38.733 |
| Avaroa 1 | Avaroa | 21° 36' 39.1" S, 67° 02' 39.7" W | cup | 18.496 | 15.655 | 38.627 |
| Avaroa 1 | Avaroa | 21° 36' 39.1" S, 67° 02' 39.7" W | cup | 18.487 | 15.641 | 38.608 |
| Avaroa 3 | Avaroa | 21° 36' 39.1" S, 67° 02' 39.7" W | cup | 18.527 | 15.659 | 38.682 |
| Avaroa 4 | Avaroa | 21° 36' 39.1" S, 67° 02' 39.7" W | cup | 18.523 | 15.635 | 38.642 |
| Avaroa 6 | Avaroa | 21° 36' 39.1" S, 67° 02' 39.7" W | cup | 18.440 | 15.650 | 38.660 |
| Avaroa 7 | Avaroa | 21° 36' 39.1" S, 67° 02' 39.7" W | cup | 18.438 | 15.584 | 38.400 |
| Avaroa 8 | Avaroa | 21° 36' 39.1" S, 67° 02' 39.7" W | cup | 18.520 | 15.632 | 38.581 |
| Avaroa 8 | Avaroa | 21° 36' 39.1" S, 67° 02' 39.7" W | cup | 18.534 | 15.644 | 38.624 |
| Avaroa 10 | Avaroa | 21° 36' 39.1" S, 67° 02' 39.7" W | cup | 18.623 | 15.667 | 38.731 |
| Location             | Details                     | Coordinates         | Type   | Lat.    | Long.    | Abbreviation |
|----------------------|-----------------------------|---------------------|--------|--------|----------|--------------|
| **Avaroa 12**        | Mantos Blancos              | 21° 37' 41.6" S, 67° 03' 15.4" W | cup    | 18.589 | 15.657   | 38.749       |
| 13M05A               |                             | bn                  |        | 18.527 | 15.641   | 38.607       |
| 13M05C               |                             | bn                  |        | 18.500 | 15.606   | 38.532       |
| 13M05F               |                             | bn                  |        | 18.492 | 15.614   | 38.554       |
| 13M05G               |                             | bn                  |        | 18.555 | 15.667   | 38.725       |
| 08M05A               | Bartola                     | 21° 42' 29.6" S, 67° 27' 34.8" W | mal + cc | 18.409 | 15.630   | 38.712       |
| 08M05B*              | bartola                     | 21° 42' 29.6" S, 67° 27' 34.8" W | cup + (mal) | 18.415 | 15.623   | 38.742       |
| 08M05C               | Bartola                     | 21° 42' 29.6" S, 67° 27' 34.8" W | mal + (cup) | 18.394 | 15.629   | 38.636       |
| 08M05D               | Bartola                     | 21° 42' 29.6" S, 67° 27' 34.8" W | cup | 18.422 | 15.642   | 38.796       |
| 08M05F*              | Bartola                     | 21° 42' 29.6" S, 67° 27' 34.8" W | cup + (cpy, mal) | 18.836 | 15.620   | 38.653       |
| 08M05J               | Bartola                     | 21° 42' 29.6" S, 67° 27' 34.8" W | cup + (mal) | 18.427 | 15.660   | 38.725       |
| 07M05A               | 25 de Julio                 | 21° 42' 52.5" S, 67° 28' 10.4" W | mal | 23.307 | 16.016   | 38.159       |
| 07M05B               | 25 de Julio                 | 21° 42' 52.5" S, 67° 28' 10.4" W | cup + (mal) | 19.719 | 15.683   | 38.112       |
| 07M05F               | 25 de Julio                 | 21° 42' 52.5" S, 67° 28' 10.4" W | mal + cup | 18.542 | 15.629   | 38.347       |
| 07M05J               | 25 de Julio                 | 21° 42' 52.5" S, 67° 28' 10.4" W | mal + az + Fe-ox | 18.496 | 15.613   | 38.293       |
| 09M05A               | Estela                      | 21° 50' 11.9" S, 67° 18' 34.6" W | cup + (mal) | 18.692 | 15.664   | 38.793       |
| 09M05C               | Estela                      | 21° 50' 11.9" S, 67° 18' 34.6" W | cup + (mal) | 18.713 | 15.688   | 38.866       |
| 09M05F               | Estela                      | 21° 50' 11.9" S, 67° 18' 34.6" W | cup + (mal) | 18.740 | 15.672   | 38.829       |
| 10M05C               | Sn Juan de Irismayu         | 22° 02' 38.7" S, 67° 08' 17.8" W | cup + (mal) | 18.569 | 15.636   | 38.581       |
| 10M05D               | Sn Juan de Irismayu         | 22° 02' 38.7" S, 67° 08' 17.8" W | cup | 18.552 | 15.621   | 38.519       |
| 10M05E               | Sn Juan de Irismayu         | 22° 02' 38.7" S, 67° 08' 17.8" W | cup | 18.668 | 15.661   | 38.660       |
| 10M05H*              | Sn Juan de Irismayu         | 22° 02' 38.7" S, 67° 08' 17.8" W | cup + (mal) | 18.560 | 15.612   | 38.524       |
| **N. Chile**         | Collahuasi                  | 20° 59' 26" S, 68° 42' 29" W | chrys  | 18.633 | 15.623   | 38.600       |
| MIT 4086             | Collahuasi                  | 20° 59' 26" S, 68° 42' 29" W | chrys + mal | 18.630 | 15.629   | 38.620       |
| MIT 4087             | Collahuasi                  | 20° 59' 26" S, 68° 42' 29" W | chrys | 18.618 | 15.602   | 38.597       |
| MIT 4088             | Collahuasi                  | 20° 59' 26" S, 68° 42' 29" W | chrys | 18.678 | 15.636   | 38.618       |
| Coll 2               | Collahuasi                  | 20° 59' 26" S, 68° 42' 29" W | chrys | 18.635 | 15.627   | 38.049       |
| Coll 8               | Collahuasi                  | 20° 59' 26" S, 68° 42' 29" W | chrys | 18.635 | 15.614   | 38.613       |
| Coll 10              | Collahuasi                  | 20° 59' 26" S, 68° 42' 29" W | chrys | 18.623 | 15.625   | 38.649       |
| Code      | Location               | Latitude | Longitude   | Mineral(s)               | Temperature | Density | Altitude |
|-----------|------------------------|----------|-------------|--------------------------|-------------|---------|----------|
| 06ML14A   | El Abra                | 21° 55' S, 68° 50' W | mal + cup       | 18.670                  | 15.616      | 38.648  |
| 06ML14B   | El Abra                | 21° 55' S, 68° 50' W | mal              | 18.576                  | 15.603      | 38.537  |
| 06ML14C   | El Abra                | 21° 55' S, 68° 50' W | chrys           | 18.710                  | 15.594      | 38.730  |
| 06ML14D*  | El Abra                | 21° 55' S, 68° 50' W | cup + bn + Cu + cpy + mal | 18.690      | 15.637      | 38.654  |
| 06ML14E   | El Abra                | 21° 55' S, 68° 50' W | turq + cup      | 18.637                  | 15.638      | 38.657  |
| MIT 4093  | Chuquicamata†          | 22° 17' 30"S, 68° 54' 30"W | enargite vein  | 18.640                  | 15.539      | 38.353  |
| MIT 5053  | Chuquicamata†          | 22° 17' 30"S, 68° 54' 30"W | enargite vein  | 18.579                  | 15.5954     | 38.498  |
| MIT 5055  | Chuquicamata†          | 22° 17' 30"S, 68° 54' 30"W | enargite vein  | 18.518                  | 15.556      | 38.423  |
| MIT 5057  | Chuquicamata†          | 22° 17' 30"S, 68° 54' 30"W | enargite vein  | 18.635                  | 15.623      | 38.565  |
| MIT 5058  | Chuquicamata†          | 22° 17' 30"S, 68° 54' 30"W | enargite vein  | 18.629                  | 15.643      | 38.645  |
| MIT 5059  | Chuquicamata†          | 22° 17' 30"S, 68° 54' 30"W | enargite vein  | 18.616                  | 15.615      | 38.516  |
| MIT 4099  | Chulaco†               | 22° 54' 29" S, 68° 11' 43.8"W | mal + qtz      | 18.742                  | 15.715      | 38.946  |
| MIT 5001  | Chulaco†               | 22° 54' 29" S, 68° 11' 43.8"W | mal + qtz      | 18.724                  | 15.696      | 38.884  |
| MIT 5002  | Chulaco†               | 22° 54' 29" S, 68° 11' 43.8"W | mal           | 18.669                  | 15.630      | 38.699  |
| MIT 5003  | Chulaco†               | 22° 54' 29" S, 68° 11' 43.8"W | mal + cup      | 18.658                  | 15.609      | 38.653  |
| MIT 5004  | Chulaco†               | 22° 54' 29" S, 68° 11' 43.8"W | cup + mal      | 18.676                  | 15.615      | 38.629  |
| MIT 5041  | Chulaco†               | 22° 54' 29" S, 68° 11' 43.8"W | mal           | 18.647                  | 15.624      | 38.653  |
| MIT 5042  | Chulaco†               | 22° 54' 29" S, 68° 11' 43.8"W | cup + mal      | 18.659                  | 15.575      | 38.608  |
| MIT 5043  | Chulaco†               | 22° 54' 29" S, 68° 11' 43.8"W | mal           | 18.598                  | 15.570      | 38.551  |
| MIT 5044  | Chulaco†               | 22° 54' 29" S, 68° 11' 43.8"W | mal           | 18.704                  | 15.667      | 38.785  |

**N.W. Argentina**

| Code      | Location               | Latitude | Longitude   | Mineral(s) | Temperature | Density | Altitude |
|-----------|------------------------|----------|-------------|------------|-------------|---------|----------|
| 06ML09A   | Pan de Azúcar          | 22° 36' 56.9" S, 66° 03' 09.1" W    | py        | 18.672      | 15.658      | 38.860  |
| 06ML09B   | Pan de Azúcar          | 22° 36' 56.9" S, 66° 03' 09.1" W    | py        | 18.659      | 15.646      | 38.811  |
| 06ML09E   | Pan de Azúcar          | 22° 36' 56.9" S, 66° 03' 09.1" W    | py        | 18.677      | 15.660      | 38.864  |
| 06ML09G   | Pan de Azúcar          | 22° 36' 56.9" S, 66° 03' 09.1" W    | py        | 18.695      | 15.679      | 38.919  |
| 06ML10A*  | Pirquitas              | 22° 41' 14.2" S, 66° 32' 38.5" W    | py        | 18.793      | 15.707      | 39.046  |
| 06ML10D   | Pirquitas              | 22° 41' 14.2" S, 66° 32' 38.5" W    | cas       | 18.844      | 15.749      | 39.185  |
| 06ML10J   | Pirquitas              | 22° 41' 14.2" S, 66° 32' 38.5" W    | py        | 18.762      | 15.682      | 38.933  |
| Code   | Region    | Coordinates       | Minerals       | Datum 1 | Datum 2  | Datum 3   |
|--------|-----------|-------------------|---------------|---------|----------|-----------|
| 06ML08C| Santana   | 23° 11' 23.3" S, 65° 11' 07.5" W | bn            | 18.353  | 15.624   | 38.457    |
| 06ML08D| Santana   | 23° 11' 23.3" S, 65° 11' 07.5" W | py + bn + mal + cpy + qtz | 18.384  | 15.655   | 38.556    |
| 06ML08E| Santana   | 23° 11' 23.3" S, 65° 11' 07.5" W | cpy + qtz + mal + az | 18.383  | 15.641   | 38.519    |
| 06ML08F*| Santana  | 23° 11' 23.3" S, 65° 11' 07.5" W | cpy + cup + bn + mal | 18.364  | 15.652   | 38.538    |
| 06ML13E| Providencia | 23° 15' 45.1" S, 66° 48' 0.4" W | cup           | 18.773  | 15.675   | 38.934    |
| 06ML13G*| Providencia | 23° 15' 45.1" S, 66° 48' 0.4" W | cup + mal     | 18.781  | 15.698   | 39.001    |
| 06ML13H| Providencia | 23° 15' 45.1" S, 66° 48' 0.4" W | cup           | 18.754  | 15.665   | 38.907    |
| 06ML03A| Cobres   | 23° 38' 54.6" S, 66° 17' 12.8" W | cup + mal     | 18.027  | 15.628   | 38.081    |
| 06ML03H| Cobres   | 23° 38' 54.6" S, 66° 17' 12.8" W | mal           | 18.005  | 15.640   | 38.037    |
| 06ML03I| Cobres   | 23° 38' 54.6" S, 66° 17' 12.8" W | mal + (cup)   | 18.008  | 15.618   | 38.034    |
| 06ML03K| Cobres   | 23° 38' 54.6" S, 66° 17' 12.8" W | cup + mal     | 17.990  | 15.622   | 38.001    |
| 06ML05E| Chorillos | 23° 59' 09.7" S, 65° 26' 12.4" W | cpy           | 18.232  | 15.655   | 38.146    |
| 06ML05H| Chorillos | 23° 59' 09.7" S, 65° 26' 12.4" W | cpy + qtz     | 18.346  | 15.631   | 38.239    |
| 06ML05G| Chorillos | 23° 59' 09.7" S, 65° 26' 12.4" W | cpy + (qtz)   | 18.433  | 15.701   | 38.402    |
| 06ML05I| Chorillos | 23° 59' 09.7" S, 65° 26' 12.4" W | cpy           | 18.342  | 15.658   | 38.231    |
| 06ML04A| Concordia | 24° 12' 02.7" S, 66° 24' 11.1" W | gn            | 18.940  | 15.681   | 39.162    |
| 06ML04B| Concordia | 24° 12' 02.7" S, 66° 24' 11.1" W | gn            | 18.923  | 15.666   | 39.148    |
| 06ML04C| Concordia | 24° 12' 02.7" S, 66° 24' 11.1" W | gn            | 18.909  | 15.674   | 39.131    |
| 06ML04D| Concordia | 24° 12' 02.7" S, 66° 24' 11.1" W | gn            | 18.924  | 15.670   | 39.137    |
| AC 915 | Taca-Taca | 24° 35' S, 67° 44' W | cpy           | 18.694  | 15.631   | 38.666    |
| AC 934 | Taca-Taca | 24° 35' S, 67° 44' W | py            | 19.182  | 15.688   | 39.105    |
| AC 950 | Taca-Taca | 24° 35' S, 67° 44' W | py            | 18.663  | 15.598   | 38.514    |
| AC 968 | Taca-Taca | 24° 35' S, 67° 44' W | mixed sulfides | 18.590  | 15.616   | 38.525    |
| AC 984 | Taca-Taca | 24° 35' S, 67° 44' W | py            | 18.687  | 15.635   | 38.654    |
| AC 986 | Taca-Taca | 24° 35' S, 67° 44' W | py            | 18.801  | 15.659   | 39.105    |
| 06ML07C| Capillitas | 27° 21' S, 66° 24' W | gn            | 18.861  | 15.669   | 38.931    |
| 06ML07F| Capillitas | 27° 21' S, 66° 24' W | gn            | 18.879  | 15.690   | 39.014    |
| 06ML07H| Capillitas | 27° 21' S, 66° 24' W | gn            | 18.819  | 15.644   | 38.842    |
Minerals listed in order of decreasing abundance in sample. Minerals listed in parentheses were present in trace amounts only. Mineral abbreviations as follows: mal = malachite, cup = cuprite, chrys = chrysocholla, bn = bornite, Cu = native copper, cv = covellite, cpy = chalcopyrite, turq = turquoise, gn = galena, az = azurite, en = enargite, cas = cassiterite, py = pyrite.

Samples were prepared for mass spectrometry by purification using standard HBr chromatography in the class 100 clean laboratory at FIU. Most sample analyses were performed by thermal ionization mass spectrometry (TIMS) on a VG354 multicollector instrument at Oak Ridge National Laboratory and on the same instrument re-installed at FIU. †Samples were analyzed using TIMS by Chempet, Inc. Samples were corrected for instrumental mass fractionation by comparison with the long-term average of replicate analyses (n>50) of the NIST SRM-981 lead isotope standard. True ratios of the SRM-981 standard were taken to be $^{206}\text{Pb}/^{204}\text{Pb} = 16.939$, $^{207}\text{Pb}/^{204}\text{Pb} = 15.484$, and $^{208}\text{Pb}/^{204}\text{Pb} = 36.712$. External reproducibility (2σ) of the lead isotope ratio measurements is taken to be better than ± 0.1% for $^{206}\text{Pb}/^{204}\text{Pb}$, ± 0.15% for $^{207}\text{Pb}/^{204}\text{Pb}$, and ± 0.2% for $^{208}\text{Pb}/^{204}\text{Pb}$; replicate analyses of individual samples were well within this range. *Data are an average of two instrumental runs.
| Mine                  | Lat. S | Long. W | Age         | Ore metals | Type/ore minerals                                      | References                                                                 |
|----------------------|--------|---------|-------------|------------|--------------------------------------------------------|----------------------------------------------------------------------------|
| **Perú**             |        |         |             |            |                                                        |                                                                            |
| San Rafael           | 14 12  | 70 24   | 23.6-22.6 Ma| Sn, Cu, Pb, Zn | Volcanic-hosted polymetallic veins with cas, cpy, sph, gn | Clark et al. (1990a), Kontak et al. (1990), Kontak and Clark (2002)        |
| Carabaya (Quenamari) | 14 15  | 70 21   | 27.1-22.6 Ma| Pb, Sn, Cu, Zn, Ag | Polymetallic veins                                      | Clark et al. (1990a), Kontak et al. (1990)                                 |
| Condoriquiña         | 14 15  | 70      | ≈25 Ma?     | Cu, Pb, Zn, Sn | Polymetallic veins                                      | Clark et al. (1990a), Kontak et al. (1990)                                 |
| Sarita               | 14 15  | 69 50   | 187 Ma      | W, Mo, Sn, Cu | Hydrothermal pipes and veins                           | Clark et al. (1990a), Kontak et al. (1990)                                 |
| Santo Domingo        | 14 15  | 70 35   | 23.2-26.1 Ma| Zn, Sn, Cu, Pb | Polymetallic veins                                      | Clark et al. (1990a), Kontak et al. (1990)                                 |
| Martha               | 14 24  | 70 25   |             | Fe, Mn, Ba   | Stratabound                                            | Clark et al. (1990a), Kontak et al. (1990)                                 |
| Rosario              | 14 27  | 70 15   |             | Mo, W, Sn, Cu | Veins                                                  | Clark et al. (1990a), Kontak et al. (1990)                                 |
| San Judas Tadeo      | 14 37  | 70 40   |             | Mo, W       |                                                        | Clark et al. (1990a), Kontak et al. (1990)                                 |
| Cecelia              | 14 37  | 69 51   | Late Paleogene | Pb, Zn, Ag | Veins and mantos of gn, sph, stan                      | Clark et al. (1990a), Kontak et al. (1990)                                 |
| Palca II             | 14 52  | 69 33   | 24-25 Ma    | W, Sn, Cu, Pb, Zn, Ag | Veins                                                   | Clark et al. (1990a), Kontak et al. (1990)                                 |
| San Isidro           | 15 00  | 69 50   |             | Ag, Sb      |                                                        | Clark et al. (1990a), Kontak et al. (1990)                                 |
| Arcata               | 15 05  | 72 20   | ≈5.5 Ma     | Ag, Au, Pb, Zn, Cu | Epithermal adularia-sericite veins with Ag sulfosalts, ac, el, sl, gn, cpy | Candiotti et al. (1990), Tosdal et al. (1995)                             |
| Cailloma             | 15 10  | 71 49   | Neogene     | Ag, Au      | Epithermal veins with td, Ag sulfosalts, gn            | Tosdal et al. (1995)                                                       |
| Orcopampa            | 15 20  | 72 20   | ≈18.8 Ma    | Pb, Zn, Ag, Au | Epithermal veins of sl, gn, td, cpy, el               | Gibson et al., 1990, Macfarlane et al. (1990)                              |
| Shila                | 15 25  | 72 10   | Neogene     | Au, Ag      | Epithermal veins with td, Ag sulfosalts, gn, el        | Tosdal et al. (1995)                                                       |
| Madrigal             | 15 37  | 71 48 42| Neogene     | Pb, Zn, Ag  | Volcanic-hosted veins                                  | Macfarlane et al. (1990)                                                   |
| Cerro Verde          | 16 31 45 | 71 36  | ≈62 Ma      | Cu, Mo, Ag  | Porphyry Cu with cpy, cc, chr, bro                     | Mukasa et al. (1990), Quang et al. (2003)                                  |
| Toquepala            | 17 16  | 70 36   | ≈57 Ma      | Cu, Mo      | Porphyry Cu with cpy, bn, mo, cc                       | Clark et al. (1990a), Clark et al. (1990b)                                 |
| Location     | Age    | Model | Metals                             | Notes                                                                 |
|--------------|--------|-------|------------------------------------|----------------------------------------------------------------------|
| Matilde      | 15 45  | 68 58 | Pb, Zn, Ag                         | Tilton et al. (1981), Macfarlane et al. (1990)                        |
| Monolito     | 15 47 24 | 68 39 | Pb                                 | Tilton et al. (1981)                                                 |
| Mercedes     | 15 52  | 68 36 18 | Cu, W, Bi                     | Tilton et al. (1981)                                                 |
| Zongo        | 16 17  | 68 08 |                                    |                                                                     |
| Don Carlos   | 16 20 42 | 68 06 54 | Ag, Cu, Pb                      | Tilton et al. (1981), this study                                    |
| Kellhuani    | 16 22 43 | 68 07 6 | Sn                                 | Lehmann (1985), Macfarlane et al. (1990)                             |
| Chojilla     | 16 24 06 | 67 46 24 | W, Sn                             | Tilton et al. (1981)                                                 |
| Quimsa Chata | 16 38 00 | 68 39 30 | Pb, Zn, Ag, Cu                   | Tilton et al. (1981), Bleiwas & Christiansen (1992), this study    |
| Urania       | 16 41 18 | 67 47 18 | W                                 | Tilton et al. (1981)                                                 |
| Viloco       | 16 51 42 | 67 30 54 | Sn, W, Mo                        | Tilton et al. (1981)                                                 |
| Caracoles    | 16 54  | 67 06 | Neogene?                          | Macfarlane et al. (1990)                                             |
| Argentina    | 16 58 54 | 67 19 48 | Sn, Zn, Bi, Cu                   | Tilton et al. (1981), Macfarlane et al. (1990)                      |
| Pacuni       | 16 59 42 | 67 19 24 | W, Sn                             | Tilton et al. (1981)                                                 |
| Pobre Cristo†| 17 00  | 67 18 |                                    | Macfarlane et al. (1990)                                             |
| Khoallaqui†  | 17 02  | 66 52 | ≈100 Ma                           | Aitcheson et al. (1995), Schultz et al. (2004)                       |
| Corocoro     | 17 10 09 | 68 27 04 | Neogene Cu                      | Bleiwas & Christiansen (1992), this study                           |
| Berenguela   | 17 18 26 | 69 08 43 | Pb, Zn, Ag, Cu, Cd               | Wallace et al. (1992), Tosdal et al. (1993)                          |
| Oruro        | 17 57 12 | 67 08 00 | Tertiary                          | Macfarlane et al. (1990), Bleiwas and Christiansen (1992)           |
| Azurita      | 18 04 06 | 68 09 22 | Neogene Cu                       | Macfarlane et al. (1990), Bleiwas and Christiansen (1992), this study |
| Cuprita      | 18 15 55 | 68 03 52 | Neogene Cu                       | Macfarlane et al. (1990), Bleiwas and Christiansen (1992), this study |
| Trinacana—Poopo† | ≈18 24 | ≈66 48 |                                    | Bleiwas & Christiansen (1992), this study                           |
| Poopo†       | 18 24  | 66 51 |                                    | Aitcheson et al. (1995)                                              |
| Negrillos†   | 18 50 26 | 68 37 42 | Neogene Pb, Zn, Ag, Cu           | Aitcheson et al. (1995)                                              |

**Notes:**
- **Tertiary**: Tertiary volcanic-hosted veins with gn, sl, cpy, td, cas, en, and complex sulfosalts.
- **Sed.-hosted cu, cup**: Sedimentary-hosted Cu, cup.
- **Shale-hosted vein**: Shale-hosted vein.
- **Epithermal veins**: Epithermal veins.
- **Epithermal veins with cpy, cas, stan, gn, sph, Ni-arsenides**: Epithermal veins with cpy, cas, stan, gn, sph, Ni-arsenides.
- **Mantos with cas**: Mantos with cas.
- **Greisen bordered veins containing wo, cas, base metal sulfides**: Greisen bordered veins containing wo, cas, base metal sulfides.
- **Epithermal volc.-hosted veins w/py, gn, sl, cpy, td.**: Epithermal volcanic-hosted veins with py, gn, sl, cpy, td.
- **Veins with wo, sch, cpy, sph**: Veins with wo, sch, cpy, sph.
- **Sulfide rich quartz veins**: Sulfide rich quartz veins.
- **Veins containing cas, sph, bis, cpy**: Veins containing cas, sph, bis, cpy.
- **Carbonatitic complex with high LREE**: Carbonatitic complex with high LREE.
- **Ss and sh-hosted Cu, cup, mal, az, ce,**: Sulfide and shoshonitic-hosted Cu, cup, mal, az, ce.
- **Sed. and volc.-hosted veins**: Sedimentary and volcanic-hosted veins.
- **Ternary volcanic-hosted veins with gn, sl, cpy, td, cas, en, and complex sulfosalts.**: Tertiary volcanic-hosted veins with gn, sl, cpy, td, cas, en, and complex sulfosalts.
- **Ss- and egl-hosted Cu, cup, Cu-oxides**: Sulfide and egl-hosted Cu, cup, Cu-oxides.
| Location                  | Latitude  | Longitude | Age (Ma) | Minerals (Pb, Zn, Ag, Sn, Cu, W, Sb) | Geology                                                                 |
|---------------------------|-----------|-----------|----------|-------------------------------------|--------------------------------------------------------------------------|
| Pumpuri†                  | 18.54     | 66.15     |          |                                     | Volcanic hosted veins and breccias with cerar, Ag, sph, gn, cpy, sulfosalts |
| Carangas†                 | 18.56 31.4| 66.37 48.2| 15.4     | Pb, Zn, Ag                          | Volcanic hosted veins and breccias with cerar, Ag, sph, gn, cpy, sulfosalts |
| India†                    | 19.00     | 66.38     |          |                                     | Aitcheson et al. (1995)                                                  |
| Mina Blanca†              | 19.05     | 66.38     |          |                                     | Aitcheson et al. (1995)                                                  |
| Mina Challachi†           | 19.05     | 66.40     |          |                                     | Aitcheson et al. (1995)                                                  |
| Santa Barbara†            | 19.08     | 66.35     |          |                                     | Aitcheson et al. (1995)                                                  |
| Malinsa†                  | 19.09     | 65.42     |          |                                     | Aitcheson et al. (1995)                                                  |
| Huari-West†               | 19.29     | 65.40     |          |                                     | Aitcheson et al. (1995)                                                  |
| Huari-Huari†              | 19.30     | 65.36     |          |                                     | Aitcheson et al. (1995)                                                  |
| Co. Huayna Tusuna Punta†  | 19.33     | 65.54     |          |                                     | Aitcheson et al. (1995)                                                  |
| Huahua                     | 19.33     | 65.42     |          |                                     | Aitcheson et al. (1995)                                                  |
| Cerro Rico de Potosi      | 19.35     | 65.45     | 13.8     | Pb, Zn, Ag, Sn, Cu, W, Sb           | Macfarlane et al. (1990): Aitcheson et al. (1995), Cunningham et al. (1996), Kamenov et al. (2002) |
| Carguaycollo              | 19.36     | 66.39     | Neogene  | Zn, Sn, Ag                          | Macfarlane et al. (1990): Aitcheson et al. (1995), Cunningham et al. (1996), Kamenov et al. (2002) |
| Tolloci†                  | 19.40     | 65.54     |          |                                     | Macfarlane et al. (1990): Aitcheson et al. (1995), Cunningham et al. (1996), Kamenov et al. (2002) |
| Gualdalupe†               | 19.41 27  | 67.42 45  | Neogene  | Cu, Ag, Au                          | Macfarlane et al. (1990): Aitcheson et al. (1995), Cunningham et al. (1996), Kamenov et al. (2002) |
| Colquechaquita            | 19.42     | 65.37     |          |                                     | Macfarlane et al. (1990): Aitcheson et al. (1995), Cunningham et al. (1996), Kamenov et al. (2002) |
| Chacacomiri               | 19.42     | 65.48     |          |                                     | Macfarlane et al. (1990): Aitcheson et al. (1995), Cunningham et al. (1996), Kamenov et al. (2002) |
| Maria Luisa               | 19.42 30  | 67.42 51  | Neogene? | Pb, Zn, Ag, Au                      | Macfarlane et al. (1990): Aitcheson et al. (1995), Cunningham et al. (1996), Kamenov et al. (2002) |
| Andacaba                  | 19.46 38  | 65.40 06  | <22 Ma   |                                     | Macfarlane et al. (1990): Aitcheson et al. (1995), Cunningham et al. (1996), Kamenov et al. (2002) |
| Kumurana†                 | 19.47 58  | 65.39 40  | <22 Ma   |                                     | Macfarlane et al. (1990): Aitcheson et al. (1995), Cunningham et al. (1996), Kamenov et al. (2002) |
| Porco                     | 19.47 57  | 65.59 17  | ≈8.6 Ma  | Pb, Zn, Ag, Sn                      | Macfarlane et al. (1990): Aitcheson et al. (1995), Cunningham et al. (1996), Kamenov et al. (2002) |
| Chinchilhuma               | 19.58 53.5| 68.21 34.5| Neogene  | Pb, Zn, Cu, Sn                      | Macfarlane et al. (1990): Aitcheson et al. (1995), Cunningham et al. (1996), Kamenov et al. (2002) |
| Veta Kholulu†             | 20.19 8.2 | 67.55 40.8| Neogene? | Cu                                  | Macfarlane et al. (1990): Aitcheson et al. (1995), Cunningham et al. (1996), Kamenov et al. (2002) |
| Location     | Lat.   | Long.  | Age (Ma) | Tectonic Setting | Geology/Mineralization                                                                 |
|--------------|--------|--------|----------|------------------|---------------------------------------------------------------------------------------|
| Pulacayo     | 20 23  | 66 42  | Neogene? | Pb, Zn, Ag, Cu, Bi | Epithermal vein with gn, sph, td, cpv, stb, jam.                                      |
| Cerro Colorado† | 20 34 17.2 | 67 59 28 | Neogene? | Cu              | Basalt-hosted veins with mal, az, cup                                                |
| Animas       | 20 55  | 66 15  | Neogene? | Pb, Zn           | Ss and sh-hosted breccia pipe with gn, sph                                          |
| Cobrizos†    | 20 59 37 | 67 12 36 | Neogene? | Cu              | Veinlets of cc, cv, Cu, cup, mal, az in Eocene sandstone and mantos in Quaternary ls.|
| San Cristobal| 20 05 18 | 67 12 19 | >8.5 Ma  | Ag, Pb, Zn       | Shallow disseminated epithermal                                                      |
| Ines†        | 21 06 08 | 67 27 12.5 | Paleogene | Cu               | ss-hosted manto with cc, ten, mal, az, chrs                                         |
| Toldos       | 21 06 40 | 67 12 20 | Neogene? | Pb, Zn, Cu, Ag   | Epithermal, volcanic hosted veins with Ag, strm, gn, sph, td, cpv, pyt, pyt          |
| Tatasi       | 21 10  | 66 10  | <16Ma    |                  |                                                                                        |
| Koholpani†   | 21 11 30 | 67 09 15 | Neogene? | Cu              | cgl.-hosted cc, mal, az                                                              |
| Eskapa†      | 21 13 49 | 67 41 56.2 | 6.3 Ma  | Cu, Ag          | Oxidized epithermal veins in biotite dacite porphyry dome w/ten, chrs, mal.          |
| Antigua      | 21 20  | 65 40  |          |                  |                                                                                        |
| Mochara      | 21 25  | 65 35  |          |                  |                                                                                        |
| Dich y Suerte† | 21 25  | 65 35  |          |                  |                                                                                        |
| Huancané†    | 21 26 10 | 66 32 44 | Neogene  | Cu              | Sed.-hosted mantos with Cu, cc, cup, ten, Cu-carbonates                             |
| Puca Mokho†  | 21 33 53 | 68 01 37.7 | Neogene? | Cu              | ss-hosted Cu, cup, mal, az                                                            |
| Escala†      | 21 35 34.7 | 66 52 8.3  | ≈18 Ma  | Pb, Zn, Ag, Cu  | Veins in altered rhyolite porphyry with gn, sph, cpv, cc, td, jam                    |
| Avaroa       | 21 36 27 | 67 02 43 | Neogene  | Cu              | ss-hosted mantos with Cu, cc, bn, cup, az, mal, ten, chr                            |
| Mantos Blancos | 21 38 39 | 67 03 13 | Neogene  | Cu              | ss-hosted mantos with , cc, bn, cpv                                                 |
| Lipiña-Galan | 21 39  | 66 21  | Miocene  |                  | Altered dacite host                                                                  |
| Bartola†     | 21 42 29.6 | 67 27 34.8 | Neogene  | Cu              | Sediment-hosted mantos with cc, mal, chr, az, cv                                    |
| Location                        | Latitude | Longitude | Age       | Minerals                        | Deposits                                                                 |
|--------------------------------|----------|-----------|-----------|---------------------------------|--------------------------------------------------------------------------|
| 25 de Julio†                   | 21 42.49 | 67 28 02  | Neogene  | Cu                              | egl-hosted veins of Cu, cup, mal, az, chr, Fe-oxides                    |
| Almacen†                       | 21 44    | 67 11     | Neogene  | Pb, Zn, Ag                      | Volcanic- and sediment-hosted veins with gn, sph                        |
| Cd. Todos Santos†              | 21 44 43 | 67 12 59  | Neogene  | Pb, Zn, Ag, Sb                  | Volcanic- and sediment-hosted veins with gn, sph, sib                   |
| Estela†                        | 21 50 11.9 | 67 18 34.6 | Neogene  | Cu                              | Stratabound mineralization                                              |
| Mesa de Plata/San Antonio de Lipez | 21 51 38 | 66 51 53  | <15Ma    | Pb, Zn, Sn, Ag, Au              | Volcanic-hosted veins with gn, cas, sph, cpy, td, Ag                   |
| Española†                      | 21 55    | 65 35     |          |                                 |                                                                          |
| San Juan de Irismayu†          | 22 02 38.7 | 67 08 17.8 | Cu       | Ss and egl-hosted veinlets with cc, cup, mal | this study                                                              |

**N. Chile**

| Location                        | Latitude | Longitude | Age       | Minerals                        | Deposits                                                                 |
|--------------------------------|----------|-----------|-----------|---------------------------------|--------------------------------------------------------------------------|
| Choquelimpie                   | 18 18 19 | 69 19 42  | ≈6.6 Ma  | Au, Ag                          | Epithermal volcano-hosted veins and breccias with electrum, arg, gn, sph, cpy |
| Tignamar/Capitana              | 18 37.4  | 69 27.4   |          | Cu, Ag, Au                      | Volcanic-hosted veins with Cu, Bi, Pb, Zn, Ag, Sb, and As sulfides       |
| Collahuasi                     | 20 59 26 | 68 42 29  | ≈33 Ma   | Cu, Mo, Ag, Au                  | Porphyry Cu-Mo deposit and associated veins with cpy, bn, mo, tn, en, cc, cv |
| El Abra                        | 21 55    | 68 50     | ≈37 Ma   | Cu, Mo, Zn, Ag                  | Porphyry Cu with cpy, bn, cc, mo, sph, td, chr, bro, cup, ten, Cu, mal, ata, ant |
| Puntillas                      | 21 58.5  | 69 48.5   |          | Pb, Ag                          | Vein                                                                     |
| Chuquicamata                   | 22 17.5  | 68 54.5   | ≈33 Ma   | Cu, Mo, Zn, Au                  | Porphyry Cu with cpy, bn, en, mo, dig, cc, cv, sl                        |
| Calama                         | 22 37.5  | 69 09.6   | Paleogene?| Pb, Ag                          | Vein                                                                     |
| Chulacaco                      | 22 54 29 | 68 11 43.8 | Cu       |                                 | Gravel-hosted Cu oxides and carbonates                                  |
| Caracoles                      | 23 3.5   | 69 0.1    | Paleogene?| Pb, Zn, Ag                      | Vein                                                                     |
| Co. Boquete                    | 23 59    | 69 29.5   |          | Pb, Ag                          | Vein                                                                     |
| Sierra Imilac                  | 24 5.7   | 68 58.5   | Paleozoic | Pb, Cu                          | Vein                                                                     |
| Chimborazo                     | 24 09    | 69 09     | ≈38 Ma   | Pb, Cu, Ag                      | Porphyry Cu                                                              |
| Escondida                      | 24 15    | 69 05     | ≈38 Ma   | Cu, Mo                          | Porphyry Cu with cpy, bn, cc, cv, en, sph, tn, gn                        |

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- Puig (1988)
- Puig (1988); Richards et al. (2001)
- Puig (1988); Padilla G. et al (2004), Richards et al. (2001)
| Location            | Latitude | Longitude | Age  | Elements | Deposit Type     | Notes                                      |
|---------------------|----------|-----------|------|----------|------------------|--------------------------------------------|
| Sierra Argomedo     | 24 42    | 68 18.5   | Triassic? | Pb, Ag, Cu | Vein             | Puig (1988)                                |
| Cachinal La Sierra  | 24 52.1  | 69 32.7   | ≈58 Ma | Pb, Cu, Ag, Au | Vein             | Puig (1988)                                |
| N.W. Argentina      |          |           |       |          |                  |                                            |
| Pumahuasi           | 22 20    | 65 35     | Ordovician | Pb, Zn    | Stratabound ores in Ordovician shale and ss with gn, sph | Puig (1988)                                |
| Cari Casini         | 22 20.88 | 65 36.0   | Ordovician | Pb, Zn    | Stratabound ores in Ordovician shale and ss with gn, sph | Zentilli et al. (1988)                      |
| La Cienaga          | 22 23.10 | 65 07.37  | Ordovician | Pb, Zn    | Stratabound ores in Ordovician shale and ss with gn, sph | Zentilli et al. (1988)                      |
| Pan de Azucar       | 22 36 56.9 | 66 03 9.1 | ≈12 Ma | Pb, Zn, Au | Volcanic-hosted veins with gn, sph | Zentilli et al. (1988), Ristorcelli and Muerhoff (2003), this study |
| Pirquitas           | 22 41 14.2 | 66 32 38.5 | Ordovician | Pb, Zn, Ag, Sn | Lower Paleozoic sediment-hosted vein with gn, sph, cas, td | Zentilli et al. (1988)                      |
| Gigante             | 23 0.50  | 65 0.88   | Ordovician | Pb, Zn    | Stratabound ores in Ordovician shale and ss with gn, sph | Zentilli et al. (1988)                      |
| Santana†             | 23 11 23.3 | 65 11 7.5 | Ordovician | Pb, Cu    | Shale-hosted veins with gn, bn, mal, az | This study                                 |
| Aguilar             | 23 11.28 | 65 41.17  | Ordovician | Pb, Zn, Ag | Stratabound ores in Ordovician sediments | Zentilli et al. (1988), Puig (1988), Macfarlane et al. (1990), Gemmell et al. (1992) |
| San Juan            | 23 14.0  | 65 24.17  | Ordovician | Pb, Zn    | Stratabound ores in Ordovician shale and ss with gn, sph | Zentilli et al. (1988)                      |
| Providencia         | 23 15 45.1 | 66 48 0.4 | Ordovician | Cu, Ag    | Sediment-hosted veins with mal, cup | Instituto de Geología y Mineralogía (1996), this study |
| Cobres†             | 23 38 54.6 | 66 17 12.8 | Ordovician | Cu       | Shallow workings of veins hosted in Ordovician granitoids, containing mal | Kirschbaum et al. (2006), this study |
| Chorillos†          | 23 59 9.7 | 65 26 12.4 | Cu         | Veins in Precambrian limestone with cpy, mal, az, chrys | Instituto de Geología y Mineralogía (1996), this study |
| Concordia           | 24 12 2.7 | 66 24 11.1 | Ordovician | Pb, Ag    | Veins in Paleozoic sediments with galena | Instituto de Geología y Mineralogía (1998), this study |
| Esperanza           | 24 14.78 | 66 28.75  | Miocene | Pb, Zn, Ag, Sn | Volcanic-hosted veins with gn, sph, cpy, td, bn | Zentilli et al. (1988)                      |
| La Armonia          | 24 19.83 | 66 49.28  | ≈10 Ma | Pb, Zn, Ag | Volcanic-hosted crustified veins with gn, sph, td, cas | Zentilli et al. (1988)                      |
| Location | Latitude | Longitude | Age (Ma) | Minerals | Type | Author(s) |
|----------|----------|-----------|----------|----------|------|-----------|
| Taca Taca | 24 35 | 67 44 | Oligocene | Cu | Porphyry copper with cpy, bn, cv, cc | Gomez and Campbell (2001), this study |
| Capillitas | 27 21 | 66 24 | 7-9 Ma | Cu, Ag, Au | Epithermal veins with rhodochrosite | Tilton et al. (1981); this study |
| Famatina | 29 01 | 67 46 | | Cu, Au | Epithermal | This study |
| Helvecia | 29 32 | 68 47 | Ordovician | Pb, Ag | Stratabound ores in Ordovician sediments | Zentilli et al. (1988) |

**Bold:** Major, regionally or globally significant mine or district  
†: small abandoned mine, prospect or mineral occurrence  
Mineral abbreviations: cpy=chalcopyrite, en=enargite, bn=bornite, cv=covellite, cc=chal cocite, dig=digenite, cas=cassiterite, mal=malachite, az=azurite, chr=chrysocholla, ata=atacamite, ant=antlerite, bro=brochantite, ten=tenorite, cup=cuprite, gn=galena, sph=sphalerite, td=tetrahedrite, jam=Jamesonite, tea=teallite, mo=molybdenite, wo=wolframite, sch=scheelite, bis=bismuthinite, strm=stromeyerite, ply=polybasite, fri=freibergite, stb=stibnite, stn=stannite, arg=argentite, aca=acanthite, stp=stephanite, el=electrum, Cu=native copper, Ag=native silver
Table 3  Lead isotope ratios of Cu-As-Ni bronze artifacts from Tiwanaku and San Pedro de Atacama

| Sample number | Artifact type | Analytical laboratory | $^{206}\text{Pb}/^{204}\text{Pb}$ | $^{207}\text{Pb}/^{204}\text{Pb}$ | $^{208}\text{Pb}/^{204}\text{Pb}$ |
|---------------|--------------|-----------------------|-------------------------------|-------------------------------|-------------------------------|
|               |              | Tiwanaku              |                               |                               |                               |
| 3951          | grapa        | FIU                   | 18.804                        | 15.704                        | 38.999                        |
| 3954          | tupu         | FIU                   | 19.050                        | 15.951                        | 39.330                        |
| 3957          | knife        | Chempet               | 18.738                        | 15.704                        | 38.905                        |
| 3965          | tupu         | Chempet               | 18.708                        | 15.680                        | 38.928                        |
| 3966          | tupu         | Chempet               | 19.234                        | 15.712                        | 38.966                        |
| 3970*         | needle       | FIU                   | 19.296                        | 15.714                        | 38.735                        |
| 3972          | needle       | FIU                   | 21.090                        | 15.830                        | 39.214                        |
| 3973          | knife        | Chempet               | 18.509                        | 15.713                        | 38.849                        |
| 3975          | knife        | Chempet               | 18.717                        | 15.678                        | 38.956                        |
| 3976          | axe          | Chempet               | 18.567                        | 15.670                        | 38.835                        |
| 3978          | ring         | FIU                   | 18.943                        | 15.721                        | 39.018                        |
| 3980          | ring         | Chempet               | 18.747                        | 15.728                        | 39.264                        |
| 3983          | nail         | FIU                   | 18.772                        | 15.673                        | 38.967                        |
| 3984          | nail         | Chempet               | 18.814                        | 15.648                        | 38.626                        |
| 3992          | cramp        | Chempet               | 18.633                        | 15.701                        | 38.845                        |
|               |              | San Pedro de Atacama  |                               |                               |                               |
| 5116          | axe          | Chempet               | 18.626                        | 15.621                        | 38.634                        |
| 5117          | axe          | Chempet               | 18.622                        | 15.618                        | 38.552                        |
| 5118          | axe          | Chempet               | 18.752                        | 15.737                        | 39.268                        |
| 5119          | axe          | Chempet               | 18.588                        | 15.654                        | 38.798                        |
| 5227          | axe          | FIU                   | 18.863                        | 15.696                        | 39.019                        |
| 5228 run 2    | axe          | FIU                   | 18.797                        | 15.708                        | 38.994                        |
| 5231          | axe          | FIU                   | 19.289                        | 15.728                        | 39.176                        |
| 5232          | axe          | FIU                   | 18.566                        | 15.694                        | 39.049                        |
| 5238          | axe          | FIU                   | 18.502                        | 15.684                        | 38.717                        |
| 5240          | axe          | FIU                   | 18.976                        | 15.710                        | 39.180                        |
| 5241          | axe          | FIU                   | 19.062                        | 15.717                        | 38.829                        |
| 5245*         | axe          | FIU                   | 18.989                        | 15.734                        | 38.803                        |
| 5246*         | axe          | FIU                   | 18.265                        | 15.633                        | 38.727                        |
| 5251*         | axe          | FIU                   | 18.608                        | 15.681                        | 38.770                        |
| 5252          | axe          | FIU                   | 18.404                        | 15.769                        | 38.920                        |
| 5254          | axe          | FIU                   | 18.707                        | 15.682                        | 38.725                        |

*Data are averages of two separate instrumental runs. Analytical methods and errors as in Table 1.
| Sample number | Location   | Item            | $^{206}\text{Pb}/^{204}\text{Pb}$ | $^{207}\text{Pb}/^{204}\text{Pb}$ | $^{208}\text{Pb}/^{204}\text{Pb}$ |
|--------------|------------|-----------------|----------------------------------|----------------------------------|----------------------------------|
| 98M05B       | Pulacayo   | galena          | 18.601                           | 15.640                           | 38.790                           |
| 98M05A       | Pulacayo   | galena          | 18.597                           | 15.648                           | 38.803                           |
| MIT 5370     | PULAC 050  | Cu mineral      | 18.631                           | 15.649                           | 38.743                           |
| MIT 5378     | PULAC 050  | furnace matte   | 18.631                           | 15.645                           | 38.829                           |
| MIT 5371B    | PULAC 050  | Cu metal        | 18.664                           | 15.677                           | 38.803                           |
| 5322         | Pulacayo   | cave artifact   | 18.654                           | 15.657                           | 38.925                           |

All analyses performed by TIMS at FIU. Analytical methods and error as in Table 1.
Table 5  Composition of copper and copper alloy artifacts from Conchopata

| Excavation Number | MIT Number | Artifact Type   | Ag  | As   | Au   | Co   | Fe   | Mn   | Ni   | Pb   | Sb   | Sn   | Zn   |
|-------------------|------------|----------------|-----|------|------|------|------|------|------|------|------|------|------|------|
| Sector A          |            |                |     |      |      |      |      |      |      |      |      |      |      |      |
| 5282              | 5282       | tupu           | 0.091 | 1.64 | n.d. | □ 0.001 | n.d. | 0.015 | 0.044 | 0.010 | 0.001 | 0.006 |
| 5283              | 5283       | tupu           | 0.139 | 0.98 | □ 0.001 | □ 0.001 | 0.013 | n.d. | 0.027 | 0.026 | 0.101 | 0.002 | 0.003 |
| 5284              | 5284       | tupu           | 0.078 | 0.72 | □ 0.001 | □ 0.001 | 0.004 | n.d. | 0.021 | 0.021 | 0.012 | 0.009 | 0.027 |
| 5286              | 5286       | tupu/pin shaft | 0.073 | 1.03 | □ 0.001 | □ 0.001 | 0.002 | n.d. | n.d. | n.d. | 0.001 | n.d. | 0.008 |
| 5287              | 5287       | tupu/pin shaft | 0.157 | 0.063 | n.d. | □ 0.001 | n.d. | n.d. | n.d. | 0.643 | 0.058 | 0.002 | 0.006 |
| 5289              | 5289       | hand tool      | 0.058 | 1.95 | □ 0.001 | □ 0.001 | n.d. | n.d. | 0.190 | 0.229 | 0.023 | 0.010 | 0.002 |
| 5290              | 5290       | hand tool      | 0.545 | 0.87 | □ 0.001 | □ 0.001 | n.d. | n.d. | 0.041 | 0.105 | 0.008 | 0.003 | 0.003 |
| 5291              | 5291       | hand tool      | 0.002 | 0.005 | 0.019 | □ 0.001 | 0.016 | n.d. | 0.183 | 0.036 | □ 0.001 | 0.005 | 0.16  |
| 5292              | 5292       | tupu head      | 0.128 | 2.29 | □ 0.001 | □ 0.001 | 0.015 | n.d. | 0.049 | n.d. | 0.005 | 0.005 | 0.008 |
| 5293              | 5293       | tupu head      | 0.088 | 0.83 | □ 0.001 | □ 0.001 | 0.001 | n.d. | 0.040 | n.d. | 0.005 | 0.002 | 0.005 |
| Sector B          |            |                |     |      |      |      |      |      |      |      |      |      |      |      |
| 5472              | 5295       | needle         | 0.059 | 1.22 | □ 0.001 | □ 0.001 | 0.002 | n.d. | 0.138 | 0.220 | 0.024 | 0.018 | 0.002 |
| 5212              | 5296       | narrow bar?    | 0.100 | 3.75 | □ 0.001 | □ 0.001 | n.d. | n.d. | 0.166 | n.d. | 0.055 | 0.002 | 0.002 |
| 262               | 5297       | hand tool      | 0.081 | 2.20 | □ 0.001 | □ 0.001 | n.d. | n.d. | 0.012 | n.d. | 0.002 | 0.002 | 0.002 |
| 5398              | 5298       | nail           | 8.06 | 0.89 | □ 0.001 | n.d. | 0.001 | n.d. | 0.074 | 0.021 | 0.010 | 0.003 | 0.002 |
| 582               | 5299       | tupu           | 0.049 | 1.13 | □ 0.001 | □ 0.001 | n.d. | n.d. | n.d. | n.d. | 0.001 | n.d. | n.d. |
| 1150A             | 5300       | tupu?          | 0.104 | 0.58 | □ 0.001 | □ 0.001 | n.d. | n.d. | 0.021 | n.d. | 0.004 | 0.002 | n.d. |
| 7082              | 5301       | unidentified   | 0.066 | 2.59 | n.d. | □ 0.001 | 0.015 | n.d. | 0.016 | 0.005 | 0.018 | 0.002 | 0.002 |
| 2392A             | 5303       | tupu?          | 0.062 | 2.72 | n.d. | □ 0.001 | n.d. | n.d. | 0.009 | 0.039 | 0.020 | 0.002 | 0.001 |
| 6022              | 5304       | mace head?     | 0.819 | 0.51 | □ 0.001 | n.d. | n.d. | n.d. | n.d. | n.d. | 0.011 | n.d. | n.d. |

Elements Ag, As, Au, Co, and Sb were determined by neutron activation.
Elements Fe, Mn, Ni, Pb, Sn, and Zn were determined by inductively coupled plasma emission spectrometry (ICP-ES).

n.d. = not detected
< 0.001 = the cut off value below which the elemental concentration was not determined.
Table 6  Lead isotope ratios of copper and copper alloy artifacts from Conchopata

| Sample number | Metal/alloy       | $^{206}\text{Pb}/^{204}\text{Pb}$ | $^{207}\text{Pb}/^{204}\text{Pb}$ | $^{208}\text{Pb}/^{204}\text{Pb}$ |
|---------------|------------------|-----------------------------------|-----------------------------------|-----------------------------------|
| Sector A      |                  |                                   |                                   |                                   |
| 5282          | Cu-As            | 18.534                            | 15.651                            | 38.563                            |
| 5283          | Cu-As            | 18.689                            | 15.650                            | 38.823                            |
| 5284          | Cu-As            | 18.881                            | 15.639                            | 39.063                            |
| 5286          | Cu-As            | 18.636                            | 15.627                            | 38.681                            |
| 5287          | Cu-Pb            | 18.762                            | 15.641                            | 38.868                            |
| 5289          | Cu-As            | 18.687                            | 15.624                            | 38.690                            |
| 5290          | Cu-As-Ag         | 18.779                            | 15.651                            | 38.872                            |
| 5290 run #2   |                  | 18.788                            | 15.662                            | 38.880                            |
| 5291          | Cu               | 18.697                            | 15.643                            | 38.743                            |
| 5292          | Cu-As            | 18.618                            | 15.630                            | 38.624                            |
| 5293          | Cu-As            | 18.532                            | 15.596                            | 38.400                            |
| 5294          | not analyzed     | 18.654                            | 15.655                            | 38.755                            |
| Sector B      |                  |                                   |                                   |                                   |
| 5295          | Cu-As            | 18.707                            | 15.640                            | 38.746                            |
| 5296          | Cu-As            | 18.777                            | 15.669                            | 38.826                            |
| 5297          | Cu-As            | 18.288                            | 15.589                            | 38.272                            |
| 5298          | Cu-As-Ag         | 18.572                            | 15.564                            | 38.433                            |
| 5299          | Cu-As            | 18.597                            | 15.600                            | 38.568                            |
| 5300          | Cu-As            | 18.506                            | 15.627                            | 38.687                            |
| 5301          | Cu-As            | 18.475                            | 15.623                            | 38.475                            |
| 5303          | Cu-As            | 18.505                            | 15.653                            | 38.554                            |
| 5304          | Cu-As-Ag         | 18.765                            | 15.663                            | 38.794                            |

All analyses performed by TIMS at FIU. Analytical methods and error as in Table 1.
| Site          | Corpus analyzed | No. determined for each metal/alloy type |
|--------------|-----------------|-----------------------------------------|
|              |                 | Cu | Cu-As | Cu-As-Ni | Cu-As-Ni-Sn | Cu-Sn |
| Conchopata   | 19              | 1  | 16    | -        | -           | -     |
| Pikillacta   | 30              | 3  | 26    | 1        | -           | -     |
| Cerro Bau’l  | 31              | 4  | 20    | 2        | 2           | 3     |
| Omo          | 4               | -  | 1     | 2        | -           | 1     |
| La Real      | 10              | 1  | 7     | 2        | -           | -     |
| Tenahaha     | 11              | -  | -     | 11       | -           | -     |