ISOTOPIC EVIDENCE FOR THE PROVENANCE OF TURQUOISE, MINERAL PAINTS, AND METALS IN THE SOUTHWESTERN UNITED STATES

by

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A Dissertation Submitted to the Faculty of the
DEPARTMENT OF GEOSCIENCES
In Partial Fulfillment of the Requirements
For the Degree of
DOCTOR OF PHILOSOPHY
In the Graduate College
UNIVERSITY OF ARIZONA

2012
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ACKNOWLEDGEMENTS

The dissertation would not have been possible without the support, cooperation, and expertise of many people and organizations. The NSF-IGERT program in Archaeological Science inspired this dissertation and provided funding during its incipient stages. The Florence C. and Robert H. Lister Fellowship provided support during its final year. Additional funding was provided by the National Science Foundation and the Dr. H. Wesley Pierce Scholarship.

Thank you to my advisor, Joaquin Ruiz, whose encouragement, expertise, and perspective helped to direct and shape my dissertation and my graduate career. I am grateful to him for the opportunity to be a part of his research group. Many thanks also go to John Chesley who was a constant source of guidance both in and out of the lab. Through our many conversations, he significantly influenced both this research and my development as a scientist. I also owe much to David Killick for assuming the role of my archaeology advisor. His unflagging enthusiasm for archaeological science and his mentorship were crucial to my developing successful collaborations with the archaeological community. I am lucky to have his support and this research bears many of his fingerprints. Jay Quade and Peter Reiners provided a much-appreciated outside perspective and I thank them for their advice and thoughtful insights over the years. The laboratory portion of this work was only possible due to the dedication and expertise of several individuals. I am especially grateful to Mark Baker, who provided countless hours of assistance, and never complained when he received panicked 3 AM phone calls from the lab. Working with him has been a great privilege and pleasure. Thank you as well to Ben McElhaney and Dave Steinke for all their work keeping the mass spectrometers whirring. Past and present members of the Ruiz Group have been wonderful lab-mates and colleagues, especially Lisa Molofsky, Tom Fenn, Molly Dendas, Jason Kirk, Ryan Mathur, Rafael del Rio Salas, and Sergio Salgado.

The specific contributions of many people and organizations to this dissertation are acknowledged within the appropriate manuscript. I’d like to give a special thank-you to Bill Baxter for being an extraordinary guide through the Cerrillos Hills many times over. Bob Downs generously allowed me to use his lab to both characterize and photograph many samples. Thank you as well to Frankie Kolb, Bernadette Thomas, Anne Chase, and all the other support staff in Department of Geosciences & College of Science, and to Cathy Snider, in the Department of Anthropology.

Throughout my time in Arizona, I learned as much from my peers as I did my professors, and I have been extraordinarily fortunate to have the friendships that supported me through the ups and downs of graduate school. I am also thankful for the encouragement and love of my family during the last 26 years of my education. My parents – Ed and Gail – were an unfailing source of support. There’s no way I would have made it this far without them. I also owe a debt of gratitude to my two Southwest “families,” the Baldwin-Zieglers and the Driscolls. Finally, I’d like to thank the Southern Arizona Roadrunners & the Work Out Group (WOG) for keeping me healthy and sane for the last 3.5 years of my Ph.D. I have learned that endurance running and graduate school have many things in common, and I am grateful for every step.
DEDICATION

This dissertation is dedicated to my parents –

who taught me the most important things I know.
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ABSTRACT

Lead and strontium isotopes are two powerful tracers that can be used to identify or constrain the provenance of a wide range of archaeological materials, but these two isotopic tracers have been rarely employed to infer the sources of artifacts in the southwestern USA. This dissertation contains four studies that demonstrate how these isotopic systems can address questions about the sources of three types of archaeological materials found in this region: turquoise, lead-based glaze-paints, and metals.

The analysis of 116 samples of turquoise from 17 deposits in the southwestern USA reveals that lead and strontium isotopes are robust and sensitive tracers of turquoise at multiple scales. Isotopic variation among turquoise deposits correlates with broad regional differences in the geologic and tectonic setting of the rocks and mineral deposits which host turquoise mineralization. Many turquoise deposits also have unique isotopic signatures that will enable insights into ancient patterns of turquoise acquisition at regional and local levels. To show the utility of these tracers when applied to archaeological turquoise, I use lead and strontium isotopic measurements to establish that the Silver Bell Mountains are the likely source of turquoise found at the Redtail site in the Tucson Basin, Arizona, USA.

This dissertation also contains new, high-precision isotopic ratios of lead ores (galena and cerrusite) from four mining districts in New Mexico, including the Cerrillos Hills. All districts studied are possible sources of lead used by Pueblo IV communities to produce glaze paints. These new measurements, made by multiple-collector ICP-MS, define the isotopic composition of the ore deposits with greater precision and accuracy than achieved in previous studies, indicating an opportunity to improve interpretations about the provenance of lead in glaze paints.

Lead isotopes are also found to be useful tools for identifying lead and copper metal associated with the 1540-1542 Vázquez de Coronado expedition. Lead shot and copper crossbow boltheads from two sites with archaeological evidence for the expedition’s presence were determined to share similar or identical lead isotopic ratios. I
propose this specific isotopic “fingerprint” can be used to identify other artifacts belonging to the expedition in the Southwest.
INTRODUCTION

Lead and strontium are among the most powerful isotopic tracers and are widely applied to problems in the field of geology, environmental science, and archaeology. In archaeology, these isotopic systems are powerful and versatile tools that can provide independent information about the provenance of a wide range of materials, including metals (Gale and Stos-Gale, 1982; Desaulty et al., 2011), glass (Henderson et al., 2005; Degryse and Schneider, 2008), glazes (Habicht-Mauche et al., 2000; Huntley et al., 2007; Iñañez et al., 2010), minerals (Farquhar and Fletcher, 1980; 1984), ceramics (Carter et al., 2011), wood (English et al., 2001; Reynolds et al., 2005), bones (Hodell et al., 2004; Grimstead, 2011), and teeth (Knudson and Buikstra, 2007). Over the past fifteen years, isotopic studies of artifact provenance have multiplied, as the advent and advancement of multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS) has provided new opportunities to pursue minimally- or non-destructive analyses (e.g. Horstwood et al., 2008; Copeland et al., 2010; Resano et al., 2010), and cheaper and more efficient ways of obtaining more precise and accurate isotopic information (e.g. Baker et al., 2006).

The Southwest United States (U.S.) and northern Mexico (a region often referred to as the “Greater Southwest”) contain a rich archaeological record, with abundant evidence for complex Prehispanic and post-contact networks of exchange that moved objects over long distances (Vokes and Gregory, 2008). Some of the materials that likely flowed through these networks, and often were moved considerable distances, include blue-green stones (turquoise, malachite, azurite), marine shells, obsidian, copper bells,
lead ore, ceramics, timber, fauna (especially macaws), and, after the arrival of the Spanish, large quantities of metal. The movement and provenance of all these materials has been addressed at various levels, with a variety of geochemical sourcing methods, and with varying degrees of success (Sigleo, 1975; Weigand et al., 1977; Mathien, 1981; Mathien and Olinger, 1992; Weigand and Harbottle, 1993; Shackley, 1995; Habicht-Mauche et al., 2000; English et al., 2001; Reynolds et al., 2005; Shackley, 2005; Huntley et al., 2007; Hull et al., 2008; Carter et al., 2011; Grimstead, 2011; Somerville et al., 2011).

This dissertation presents new ways in which high-precision measurements of lead isotopic ratios (by MC-ICP-MS) and strontium isotopic ratios (by thermal ionization mass spectrometry, TIMS) can be used to gain information about the provenance of archaeological materials in the Greater Southwest. The studies contained herein address the provenance or origin of metals (Appendix A), turquoise (Appendices B and C), and lead-based mineral paints (Appendix D). Collectively, they reveal the enormous potential for lead and strontium isotopic analysis to provide new knowledge about the sources of these materials and to thus inform our knowledge of the social, political, and economic networks that mediated the exchange and movement of both objects and people across the Greater Southwest.
PRESENT STUDY

The methods, results, and conclusions of this study are presented as four papers appended to this dissertation. All papers are co-authored, but I am the senior author on all of them, and carried out the isotopic measurements reported therein. In these studies, my co-authors and I present new evidence that clearly shows high-precision lead and strontium isotopic measurements can effectively be applied to investigate the provenance of inorganic materials found in the archaeological record of the southwestern United States (U.S.). Specifically, we establish that these tools can be applied to infer the provenance of metals, turquoise, and lead-based mineral paints. Because these materials were moved over long distances, the results of the present study create new opportunities for addressing archaeological questions about social and economic networks, exchange, resource acquisition, and cultural contacts across the Southwest U.S. and beyond.

In Appendix A, we propose that lead isotopic analysis may provide a new way to identify material culture associated with the expedition of Francisco Vázquez de Coronado, which traveled across the present-day southwestern U.S. and northern Mexico from 1540 to 1542. Presently, archaeological evidence of the expedition is scarce, and many details of its route though Sonora, Arizona, New Mexico, Texas, and Kansas remain controversial. Poor knowledge of the expedition’s route partly stems from its limited archaeological footprint and the overprint of these material traces by subsequent centuries of Spanish occupation and activity (Rhodes, 1997). Until now, identifying archaeological evidence of the expedition has required the presence of one or more of the small number of artifacts considered diagnostic of the 1540’s: crossbow parts and
Accessories, copper and brass aglets (lace tips), Nueva Cadiz glass beads, sheet-brass “Clarksdale” bells, and obsidian-edged swords (Flint, 1997; Rhodes, 1997). These artifacts, however, are rare, and have only been found in a few archaeological sites.

Appendix A presents lead isotopic ratios of both lead and copper-based metallic artifacts recovered from two sites that are widely accepted as having material evidence for the expedition: Piedras Marcadas Pueblo, in present-day Albuquerque, New Mexico, and the Jimmy Owens Site, south of present-day Floydada, Texas (Blakeslee and Blaine, 2003; Schmader, 2011). Twenty-six artifacts from these two sites were included in the study, including four copper crossbow boltheads, one probable copper crossbow bolthead with a “conical” shape, thirteen lead balls (shot), four fragments of lead metal with no recognizable shape, and three scraps of copper sheet. These are the first isotopic measurements applied to artifacts likely to be associated with the Coronado expedition.

This study’s key finding is the observation that the same classes of artifacts from each site – primarily copper crossbow boltheads and fragments of lead shot – have similar or overlapping lead isotopic ratios. The average lead isotopic ratios of the four copper crossbow boltheads (two from each site) are: \(^{206}\text{Pb}/^{204}\text{Pb} = 18.711 \pm 0.034\) (1\(\sigma\)), \(^{207}\text{Pb}/^{204}\text{Pb} = 15.653 \pm 0.001\) (1\(\sigma\)), \(^{208}\text{Pb}/^{204}\text{Pb} = 38.64 \pm 0.040\) (1\(\sigma\)). The average lead isotopic ratios for twelve lead balls we attribute the Coronado expedition (four from the Jimmy Owens Site and eight from Piedras Marcadas Pueblo) are: \(^{206}\text{Pb}/^{204}\text{Pb} = 18.754 \pm 0.025\) (1\(\sigma\)), \(^{207}\text{Pb}/^{204}\text{Pb} = 15.656 \pm 0.005\) (1\(\sigma\)), and \(^{208}\text{Pb}/^{204}\text{Pb} = 38.732 \pm 0.017\) (1\(\sigma\)). The isotopic correspondence among similar artifacts from both sites leads us to conclude that these objects originated with the Coronado expedition and that their isotopic ratios
are characteristic of the copper metal and lead shot carried and used by Coronado and his men. Thus, where lead and/or copper metal is present at a site where evidence for the expedition’s presence is ambiguous, we propose that lead isotopic analysis can be applied as tool to better evaluate the possibility it contains physical remnants of the Coronado expedition. This result is particularly significant since lead shot would otherwise be a non-diagnostic type of artifact that could not be used to either bolster or refute claims for the Coronado expedition’s presence at specific archaeological sites.

Appendices B and C present evidence that lead and strontium isotopic ratios are sensitive and effective indicators of turquoise provenance across the southwestern United States and northern Mexico. While the other studies in this thesis (Appendices A and D) provide insight into objects that were exchanged or moved over restricted periods of time or across limited areas, turquoise is a material that can inform us about patterns of acquisition and exchange over a much wider range of temporal and spatial scales. In Precolumbian North America, it was mined over an area that includes much of Arizona, New Mexico, southeastern California, Nevada, Colorado, and Sonora and Zacatecas in Mexico (Blake, 1858; Hidden, 1893; Paige, 1912; Crawford and Johnson, 1937; Morrissey, 1968; Leonard and Drover, 1980; Weigand and Harbottle, 1993; Milford, 1995; Mathien, 1998). Because it was likely exchanged over long distances (perhaps as far as from the American Southwest to Mesoamerica), tracing turquoise requires finding a geochemical technique that can distinguish among numerous and distant sources of the mineral.
In Appendix B, we directly apply lead and strontium isotopes to interpret the provenance of turquoise in an archaeological setting. We report lead and strontium isotopic ratios of turquoise artifacts recovered from two archaeological sites in Arizona. The first is the Redtail Site, a community in the northwestern part of the Tucson Basin, where over 3000 fragments of turquoise were recovered from what appears to be an early Hohokam workshop (Bernard-Shaw and Hohmann, 1989). The second site lies about 30 miles to the northwest and consists of two pit houses and the remains of several brush structures (Slawson, 1997). This site, called Scorpion Village, is located close to Prehispanic turquoise mines along El Tiro Wash, on the periphery of the Silver Bell Mountains. Turquoise excavated from these structures is inferred to represent material extracted from these mines in prehistory.

Ceramics reveal that both sites were occupied during the early Colonial Period (~760-820 AD), leading archaeologists to suggest that turquoise at Redtail was mined in the Silver Bells (Vokes and Gregory, 2008). In Appendix B, we test this idea by comparing the lead and strontium isotopic compositions of ten samples of turquoise from Scorpion Village with the lead and strontium isotopic compositions of seventeen samples from the Redtail site. We find the range of both lead and strontium isotopic compositions measured on artifacts from each site are similar, and plot together using any combination of isotopic ratios. Furthermore, these measurements contrast with those of other sources across the Southwest, as described in Appendix C. This study presents the first geochemical evidence for the presence of turquoise from the Silver Bell Mountains in an archaeological site, and indicates the Silver Bells may have supplied turquoise that
moved through early Hohokam trade networks (Vokes and Gregory, 2008). The correspondence of the inferences drawn from the isotopic data with prior archaeological expectations establishes that lead and strontium isotopes provide the information necessary to correctly infer the provenance of turquoise artifacts.

Appendix C presents the results of lead and strontium isotopic analyses on over 116 samples of turquoise from 17 sources of the mineral across most of the Southwest U.S and northern Mexico. We particularly focus on sources in Arizona, New Mexico, southern Colorado, southern Nevada, and southeastern California, where evidence of Prehispanic mining has been documented. These analyses form the largest published geochemical dataset on turquoise to date (for other published geochemical data on turquoise, see: Sigleo, 1975; Mathien and Olinger, 1992; Hull et al., 2008). The primary finding of Appendix C is that, when used together, lead and strontium isotopic ratios are effective discriminators of turquoise sources and differentiate between them at multiple scales. On the largest scale, we observe that isotopic variation among turquoise sources correlates with broad regional differences in the geologic and tectonic setting of the rocks and mineral deposits which host turquoise mineralization. As a result, isotopic signatures of turquoise deposits vary geographically. Because turquoise may have been traded over long distances, the geographic grouping of isotopically similar sources should permit useful archaeological interpretations about provenance even if an artifact has a signature that overlaps with more than one source area. Furthermore, the link between the geologic setting of turquoise sources and their isotopic compositions will permit geologically-based inferences about the potential source region of turquoise artifacts, even if their
isotopic composition does not fall within the range of a known source. No previous study of turquoise provenance has been able to define meaningful relationships between the geologic setting and isotopic composition of turquoise deposits, and this feature makes our study unique (Sigleo, 1975; Weigand et al., 1977; Mathien and Olinger, 1992; Weigand and Harbottle, 1993; Hull et al., 2008).

At a finer scale, many of the turquoise deposits examined in Appendix C have distinctive isotopic signatures that should allow more nuanced interpretations of provenance, and enable insights into patterns of acquisition and exchange over regional and local scales. Significantly, one of these source areas is the Cerrillos district, thought to be the largest and most important source of turquoise in Prehispanic North America (Warren and Mathien, 1985; Mathien, 1998). A distinctive fingerprint for this source is significant because it will enable future research to test many previous ideas about the distribution of Cerrillos turquoise in the archaeological record, including its presumed presence in Chaco Canyon and in Mesoamerica (Harbottle and Weigand, 1992; Weigand, 1992; Weigand and Harbottle, 1993; Mathien, 2001).

In a few cases, we are able to show that lead and strontium isotopic ratios provide distinctive fingerprints for specific areas of ancient mining within larger source areas. Among our analyses, we single out two areas within the Cerrillos district (Mt. Chalchihuitl and Turquoise Hill) and two areas within the Mineral Park district (Turquoise Mountain and Ithaca Peak), each with well-documented evidence of intensive ancient mining activity (Blake, 1858; Harbottle and Weigand, 1992; Weigand, 1992; Weigand and Harbottle, 1993; Milford, 1995; Mathien, 1998; 2001). Our measurements
indicate that turquoise at each of these locales has distinctive isotopic ratios, and thus reveal the possibility of pinpointing the source of some turquoise artifacts at the sub-deposit scale. While it is possible that future measurements may expand the “fingerprints” for turquoise sources examined in this study, or identify other sources with non-unique isotopic signatures, the large number of samples in our study constitute strong evidence that lead and strontium isotopes will remain powerful tools with which to interpret turquoise provenance.

Appendix D presents new, high precision lead isotopic ratios on lead ores that may have been used by Pueblo groups in central New Mexico and eastern Arizona to create glaze paint decorations on ceramic bowls between 1275 and 1700 AD. From an archaeometric perspective, these glaze wares are a noteworthy category of artifact, because (with the exception of the studies presented in this dissertation) they are the only type of artifact in the Southwest U.S. that has been previously studied with lead isotopic analysis (Habicht-Mauche et al., 2000; 2002; Nelson and Habicht-Mauche, 2006; Huntley et al., 2007; Aggarwal et al., 2008; Huntley, 2008). However, despite intensive study and hundreds of isotopic analyses, interpretations about the sources of lead ore used by Pueblo potters remain tentative because the isotopic signatures of glaze paints often did not match those of ore sources and because multiple ore sources were found to have overlapping isotopic ratios (Huntley et al., 2007; Huntley, 2008).

In Appendix D, we posit that some of these interpretative difficulties could be resolved by re-evaluating both ores and artifacts with higher precision measurements of lead isotopic ratios. Previously, isotopic measurements of lead ore and glaze paints have
been made using magnetic sector single collector high resolution-inductively coupled plasma-mass spectrometry (HR-ICP-MS) (see Habicht-Mauche et al., 2002 and Huntley et al., 2007, for a description of the methods). Typical errors reported with these measurements range up to 0.5% (Huntley et al. 2007). These are an order of magnitude higher than precisions typically achievable using multi-collector (MC)-ICP-MS (Rehkämper and Halliday, 1998; Rehkämper and Mezger, 2000; White et al., 2000; Woodhead, 2002).

We address this lack of high-precision data by re-analyzing ores from possible sources in New Mexico’s Rio Grande Valley using multi-collector-ICP-MS. Typical errors on $^{206}\text{Pb}/^{204}\text{Pb}$ ratios measured in our study range between 0.02 and 0.04% and are about an order of magnitude more precise than previously reported ratios. Our dataset, which consists of a subset of the same samples measured in previous studies (e.g. Huntley et al. 2007; Habicht-Mauche et al. 2002) includes thirty-two samples of galena from the Cerrillos district (from eleven different mines across the district), four samples of cerrusite from the Magdalena district, nine samples from the Hansonburg district, and one sample from the Joyita Hills. Our extensive analysis of ores from the Cerrillos district reflects its importance to studies of glaze paint provenance, as it contains the only well-documented ancient lead mines in the Southwest U.S. (Mathien, 1998; Habicht-Mauche et al., 2000; Bice et al., 2003).

In contrast to previously published values (Habicht-Mauche et al., 2002), our data reveal a much narrower range of ratios associated with Cerrillos ores and show no variation between mines located in the northern or southern part of the mining district. In
total, $^{206}\text{Pb}/^{204}\text{Pb}$ ratios vary between 18.508-18.753, $^{207}\text{Pb}/^{204}\text{Pb}$ ratios vary between 15.580-15.608 and $^{208}\text{Pb}/^{204}\text{Pb}$ ratios vary between 38.388 -38.560. These data, when plotted in $^{207}\text{Pb}/^{204}\text{Pb}$ vs. $^{206}\text{Pb}/^{204}\text{Pb}$ space, define an array with a slope of 0.1047, which correlates with a model age of about 1.7 Ga. This slope is very different from the slope of the previously reported ratios, which was considerably steeper (~0.7, see Habicht-Mauche et al., 2002). The re-definition of the slope formed by Cerrillos ores is important because interpretations about the provenance of many glaze paints have been partly based on the widely different trends formed by data published on the Cerrillos district (Habicht-Mauche 2000; 2002) when compared with data published on other ore deposits in New Mexico (Stacey and Hedlund, 1983; Huntley et al., 2007). In addition to revising the isotopic signature of the Cerrillos district, we are able to refine signatures for other sources (Magdalena, Hansonburg, Joyita Hills) as well. We also make a case that previous data sets contained several mislabeled museum samples and inaccurate isotopic measurements which have further confounded interpretations about the provenance of lead ore contained in glaze paints.

In sum, Appendix D provides much more precise and accurate isotopic ratios for deposits of lead ore potentially used by Pueblo potters in the late prehistoric and Protohistoric periods. We use these data to show that clearer interpretations of isotopic ratios in glaze paints should be possible because ore sources have discrete and restricted isotopic signatures. If high-precision measurements are applied to glazes in future studies, we predict that it will be possible to (1) definitively link more glazes to ore sources, (2) evaluate the possibility the glazes were made with ore from deposits not
sampled, and (3) determine if the isotopic composition of a glaze is the result of mixing of ore from two or more sources.
REFERENCES


Hidden, W.E., 1893. Two new localities for Turquoise. American Journal of Science 392,


Rhodes, D.L., 1997. Coronado fought here: crossbow boltheads as possible indicators of


APPENDIX A: LEAD ISOTOPE ANALYSIS AS A NEW METHOD FOR IDENTIFYING MATERIAL CULTURE BELONGING TO THE VÁZQUEZ DE CORONADO EXPEDITION

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LEAD ISOTOPE ANALYSIS AS A NEW METHOD FOR IDENTIFYING MATERIAL CULTURE BELONGING TO THE VÁZQUEZ DE CORONADO EXPEDITION

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Abstract

Archaeological evidence has become an increasingly important component of efforts to identify the route of the Francisco Vázquez de Coronado expedition through northern Mexico and the southwestern United States (1540-1542). Here, we report the first high-precision lead isotopic measurements of artifacts from two archaeological sites with strong material evidence for the expedition’s presence: Piedras Marcadas Pueblo in New Mexico and the Jimmy Owens Site in Texas. The analysis of lead and copper armaments from both sites reveals that many artifacts have overlapping or extremely similar isotopic ratios. We propose that the narrow range of lead isotopic ratios measured on these artifacts can be interpreted as a geochemical fingerprint for some of the Coronado expedition’s surviving material culture, and provides evidence that we interpret to suggest the expedition derived lead and copper metal from Mexican sources. Such a geochemical fingerprint presents an empirical method for discriminating between artifacts that belonged to the Coronado expedition and those related to subsequent Spanish, historical, or modern activity in the Southwest U.S. Thus, this method could
significantly impact the search for and identification of archaeological sites associated with the Coronado expedition.

1. Introduction

From 1540 to 1542, Francisco Vázquez de Coronado and the members of his entrada trekked through areas of present-day Sonora, Arizona, New Mexico, Texas, and Kansas. An enormous undertaking, the Coronado expedition comprised several hundred European men, hundreds of slaves, over a thousand native Mexica, Tlaxcalan, Tlatelolcan and Tarascan soldiers, and an unknown number of women and children. It was the first major European incursion into the present-day Southwest United States (U.S.). Most of our knowledge of the expedition, and of its interactions with indigenous groups, comes from documents that were prepared before, during, or in the aftermath of the entrada’s two-year journey (Flint and Flint, 2005). To understand the consequences of these encounters, it is necessary, at a minimum, to know where the expedition traveled. Historical documents pertaining to the entrada place it in Mexico City, Compostela, Culiacán, the Zuni ancestral sites of Hawikku, Kechiba:wa, and Mats’a:kyá, the El Morro-Malpais area, Acoma, Zia, Galisteo, the Rio Grande Pueblos from Isleta to Taos, Pecos Pueblo, and central Kansas (See Sanchez, 1997a, b, c, d for a summary; Flint and Flint, 2005). However, much of the expedition’s path remains unknown, and even a broad corridor encompassing the lines of march cannot be drawn with confidence (Sanchez, 1997c). This uncertainty derives, in part, from the sometimes contradictory and often vague nature of the names and descriptions of key topographic features, landmarks, and settlements encountered by the expedition (Polzer, 1997).
Given the inherent limitations of the documentary evidence, archaeological research has emerged as central to the study of the Coronado expedition’s route. However, due to the intensity of Spanish activity in the Southwest during the 16th and 17th centuries, physical traces of Vázquez de Coronado and his men are difficult to isolate and identify with certainty. The expedition’s short-term encampments have left limited archaeological traces on the modern landscape, and much of its surviving material culture is difficult to distinguish among that left by several centuries of subsequent Spanish occupation and activity (Rhodes, 1997). Currently, linking archaeological sites with the Coronado entrada requires the presence of one or more of a very limited set of artifacts carried by Vázquez de Coronado and his men, but not believed to have been brought into the Southwest by later Spanish explorers and settlers. These objects, broadly (but not universally) considered to be indicative of the Coronado expedition’s presence, include: crossbow parts and accessories, copper and brass aglets (lace tips), Nueva Cadiz glass beads, sheet brass “Clarksdale” bells, and obsidian-edged swords (Flint, 1997; Rhodes, 1997). Unfortunately, these diagnostic artifacts are rare, and, in some cases, may have been moved, redistributed, or traded by native groups after the expedition’s departure. Thus far, physical evidence of the expedition has only been identified at a few archaeological sites including: Hawikku (Damp, 2005), Kechiba:wa: (Mathers et al., 2009), Santiago Pueblo (Vierra, 1989; Vierra and Hordes, 1997) Piedras Marcadas Pueblo (Schmader, 2008a, 2008b, 2009, in press), Pecos Pueblo (Kidder, 1932), the Jimmy Owens Site (Blakeslee et al., 1997; Blakeslee and Blaine, 2003), and at several sites in Kansas (Wedel, 1990). In order to better recognize archaeological traces of the
Coronado expedition, researchers need new ways to identify other artifacts that may be directly associated with it. We propose that lead isotopic analysis can be applied to metallic artifacts to help evaluate whether or not they belonged to the Coronado entrada.

2. Approach

Lead (Pb) isotopic analysis is typically used in archaeology to identify or constrain the geologic provenance of a wide range of metals, minerals, and other material (such as glass) recovered from archaeological contexts (e.g., Brill and Wampler, 1967; Gale and Stos-Gale, 1982; Habicht-Mauche et al., 2000; Niederschlag et al., 2003; Thibodeau et al., 2007). While inferences regarding geologic provenance are relevant to this study, our principal objective is not to link metallic artifacts with a specific country, region, mining district, or ore deposit. Instead, our primary goal is to compare the lead isotopic signatures of metallic lead and copper-based objects recovered from two different archaeological sites associated with the Coronado expedition.

This comparison is driven by the hypothesis that many of the metallic armaments associated with the expedition may have similar or even overlapping lead isotopic ratios. This isotopic consistency would be expected if the expedition’s supply of lead and/or copper metal was produced from ores derived from a specific area or mine, or simply from specific batch(es) of smelted metal. If this hypothesis is correct, these metallic objects should have a similar or identical range of lead isotopic compositions. Such a characteristic range of isotopic ratios would effectively constitute a geochemical “fingerprint” that could be used to identify material culture associated with the entrada.
The muster roll for the expedition indicates that at least 20 crossbows and 25 arquebuses were among the weapons carried by it (Flint and Flint, 2005). Thus, to test our hypothesis, we apply lead isotopic analysis to lead shot, copper crossbow boltheads, and copper sheet recovered from two well-documented archaeological sites associated with the Coronado expedition: Piedras Marcadas Pueblo (New Mexico Laboratory of Anthropology site number 290) and the Jimmy Owens Site (41FL81) (Fig.1). Piedras Marcadas is one of at least eleven Tiguex pueblos occupied in the 16th century and is located in the present-day Albuquerque-Bernalillo area of New Mexico (Barrett, 2002). The Jimmy Owens Site, located in Blanco Canyon, south of Floydada, Texas is a probable campsite occupied by the expedition as it traveled north to Quivera (Blakeslee and Blaine, 2003; Blakeslee et al., 1997). If lead and/or copper artifacts from both sites share a similar range of lead isotopic ratios, it would support our hypothesis and provide a basis to evaluate whether or not lead isotopes can provide a viable ‘fingerprint’ for the expedition’s material culture (Haecker, 2008).

A geochemical fingerprint would be most useful if applicable to artifacts that do not have any external characteristics to indicate their association. Lead balls, usually identified as lead shot, make up the majority of objects in our sample set. These are common artifacts in colonial contexts of the Southwest, but tend to be devoid of external features that could link them to a particular time period or to the different groups that may have produced or used them. However, lead isotope analysis can provide identifying information on these otherwise non-diagnostic objects. For example, the isotopic ratios of lead balls from 18th century forts in Texas and Oklahoma make it possible to
differentiate between ammunition produced by the Spanish, and that used or manufactured by the French (Schooler, 2009). In much the same way, the characterization of a specific isotopic fingerprint associated with the Coronado expedition’s lead supply could have a major impact on archaeological efforts to find material traces of the expedition (Haecker, 2008).

The inclusion of copper crossbow boltheads (also known as quarrels) in our sample set is also of particular relevance. Crossbow boltheads are metal tips or projectile points that are attached to the crossbow arrow shaft (bolt). A common weapon in medieval Europe and a staple of early Spanish warfare in the New World, the crossbow began to be phased out during the mid-16th century as arquebuses and other more advanced gunpowder firearms took its place (Rhodes, 1997; Gagné, 2003). Although it is conceivable that the much smaller Chamuscado-Rodriguez (1581-1582) and Espejo (1582-1583) expeditions may have carried crossbows into New Mexico during the 1580’s (Gagné, 2003), all known crossbow boltheads in the Southwest are attributed to the Coronado expedition. Thus, crossbow quarrels provide a critical point of reference. The analysis of multiple boltheads from two distant archaeological sites (Piedras Marcadas Pueblo and the Jimmy Owens Site) provides a direct test of our hypothesis that these objects should have similar lead isotopic compositions and simultaneously provides constraints regarding the geologic provenance of the copper ore deposit(s) that supplied the expedition. Ideally, if the specific lead isotopic signature of the boltheads could be tied to that of other, less restrictive objects (e.g. copper sheet), it would also provide an
opportunity to identify material culture associated with the expedition, even where copper crossbow boltheads are not present.

We acknowledge that both Piedras Marcadas Pueblo and the Jimmy Owens Site have complex and different occupational and post-occupational histories and that metallic artifacts recovered from these locations may be of varying age. However, there is currently no documented evidence of 17th, 18th, or 19th century occupation or activity at Piedras Marcadas Pueblo, and it has been argued that metallic artifacts recovered from the site are all either 16th or 20th century in age (Schmader, in press). The strong evidence for the Coronado expedition’s presence at both sites combined with the availability of diagnostic and non-diagnostic artifacts for isotopic analysis presents a unique opportunity to search for a possible isotopic fingerprint of the entrada.

3. Materials and methods

To test our hypothesis, we measured lead isotopic ratios of 26 lead and copper objects. Seventeen are artifacts recovered from Piedras Marcadas Pueblo and nine are artifacts associated with the Jimmy Owens Site (Table 1). Analyzed samples from Piedras Marcadas Pueblo include: two copper crossbow boltheads, one possible copper crossbow bolthead, three fragments of copper sheet, and nine lead balls which have a range of sizes and are variably spherical, flattened, or otherwise misshapen. In addition, we analyzed two samples of lead metal that have no identifiable shape. From the collection associated with the Jimmy Owens Site, we sampled two copper crossbow boltheads, four lead balls, and two shapeless lead fragments (one was labeled as “lead sprue” and other as “melted lead”). For comparative purposes, we also analyzed a
flattened projectile from the Jimmy Owen Site that was identified as a .45 caliber pistol bullet dating to the late 19th century (Charles Haecker, personal communication, December 13th, 2010). In addition to this data set, we include the isotopic measurements on a single fragment of copper metal recovered from the surface of Calabacillas Pueblo in New Mexico (see Section 6 for discussion).

Copper samples were removed with a Dremel tool, using a new carbide drill bit for each sample. Care was taken when drilling to remove and avoid any corrosion and to only drill fresh metal. However, to assess the effect corrosion may have on the isotopic signature of the copper objects, we separately analyzed corrosion from a piece of copper sheet, as well as copper shavings from two of the crossbow boltheads that contained bits of corrosion (Table 1). Between 10 and 25 mg of copper metal was drilled from each copper object. Fig. 2 shows a fragment of copper sheet (PM-986) after the sample was removed. The quantity of copper metal (or any material) needed for lead isotope analysis depends upon the concentration of lead in a given sample. Ideally, we aim to recover at least 50 ng of lead for analysis. The 10-25 mg of copper shavings collected for each sample was based on our estimate that the copper objects contained at least 2-5 ppm (parts per million) of lead. All acid solutions used during sample preparation and analysis were made from twice-distilled acid and ultrapure Milli-Q water (Millipore, 18.2 MU). For each sample, all copper shavings were dissolved in 8 M nitric acid. After dissolution, lead was separated from copper and other elements using Sr-Spec resin.

Lead objects were sampled by running a clean cotton or polyester-tipped swab (CleanTips Polyester Alpha Mini Swab, ITW Texwipe) over the surface of each object.
The sampled surface was first cleaned with a swab dipped in a solution of 2% nitric acid, and where possible, efforts were made to expose a small spot of corrosion-free lead metal. Next, a second swab was dipped in a clean 2% nitric acid solution and run across the same surface. This swab was stored in a dry Falcon tube until analysis. To prepare the sample, the tip of the swab was soaked in 2% nitric acid (~1 mL) for 1-5 min to remove lead. The swab was then discarded. Using 2% nitric acid, all samples were diluted to a lead concentration of approximately 50-100 ppb (parts per billion) for analysis. We chose to sample the lead objects using a swab because it is minimally invasive and provides a simple, rapid, portable, and relatively inexpensive method of sample preparation.

Lead isotope analysis was conducted on a GV-Instruments multi-collector inductively coupled mass spectrometer (MC-ICPMS) at the University of Arizona. Before analysis, all samples and standards were spiked with thallium (Tl) to achieve a Pb:Tl ratio of approximately 10. All measurements were mercury(Hg)-corrected and empirically normalized to Tl using the exponential law correction after methods developed by Rehkämper and Mezger (2000). To correct for interlaboratory bias, all results are normalized to the values reported by Galer and Abouchami (1998) for the NBS-981 standard. Both internal and external errors were calculated for each sample.

Internal error reflects the reproducibility of the measurements on individual samples, whereas external errors are derived from the long-term reproducibility of the NBS-981 standard, and result in part from mass bias effects within the instrument. In the case of all analyses included in this study, the external errors exceed the internal errors, and
therefore are the errors reported here. Over the course of the seven analytical sessions in which data was collected, the external errors ranged between 0.006% and 0.031% for $^{206}\text{Pb}/^{204}\text{Pb}$, 0.009%-0.034% for $^{207}\text{Pb}/^{204}\text{Pb}$, and 0.017%-0.043% for $^{208}\text{Pb}/^{204}\text{Pb}$. Total process blanks were measured alongside samples to assess contamination introduced from laboratory procedures. Total process blanks contained between 50 and 200 pg of lead, an insignificant proportion of the total lead extracted from each sample.

4. Results

The main objective of this study is to compare the lead isotopic compositions of lead and copper metal objects from Piedras Marcadas Pueblo to the lead isotopic compositions of similar artifacts associated with the Jimmy Owens Site. The isotopic ratios of all artifacts analyzed are reported in Table 1 and graphically presented in Figs. 3 and 4. One primary observation we make from this data set is that the majority of metallic lead artifacts tested from both sites have very similar or overlapping lead isotopic ratios. These objects include seven fragments of lead shot from Piedras Marcadas Pueblo and five fragments of lead shot from the Jimmy Owens Site. Taken together, the lead isotopic ratios of these objects range from 18.738 to 18.833 for $^{206}\text{Pb}/^{204}\text{Pb}$, 15.651-15.670 for $^{207}\text{Pb}/^{204}\text{Pb}$, and 38.716-38.776 for $^{208}\text{Pb}/^{204}\text{Pb}$ (Table 1, Figs. 3 and 4). Likewise, we also observe that the isotopic ratios of two copper crossbow boltheads from Piedras Marcadas Pueblo (PM-40 and PM-865) are very similar to those of two copper crossbow boltheads associated with the Jimmy Owens site (JOS-10 and JOS-31). The lead isotopic ratios of these four boltheads range between 18.670 and 18.750 for $^{206}\text{Pb}/^{204}\text{Pb}$, 15.6520-15.654 for $^{207}\text{Pb}/^{204}\text{Pb}$, and 38.611-38.700 for $^{208}\text{Pb}/^{204}\text{Pb}$. 
(Table 1, Fig. 3). Additionally, the isotopic compositions of the boltheads are very similar to (and overlap with) the range of isotopic ratios measured on many of the lead objects. When taken all together, one of the most striking characteristics of these lead and copper artifacts is that they all have very nearly identical $^{207}\text{Pb}/^{204}\text{Pb}$ ratios within the precision of our measurements (Table 1; Fig. 3).

Aside from two crossbow boltheads discussed above, no other copper artifacts were tested from the Jimmy Owens Site. However, four additional copper artifacts were measured from Piedras Marcadas Pueblo. These artifacts consist of one possible crossbow bolthead and three pieces of copper sheet. These artifacts have lower $^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$, and $^{208}\text{Pb}/^{204}\text{Pb}$ ratios than the other four boltheads and have $^{207}\text{Pb}/^{204}\text{Pb}$ ratios that are analytically identical to one another. The ranges of measured ratios on these objects are 18.417-18.672 for $^{206}\text{Pb}/^{204}\text{Pb}$, 15.619-15.625 $^{207}\text{Pb}/^{204}\text{Pb}$, and 38.421-38.540 for $^{208}\text{Pb}/^{204}\text{Pb}$. Furthermore, within measurement errors, the possible bolthead (PM-607) is an exact isotopic match for one of the pieces of copper sheet (PM-986; Table 1, Fig. 4). None of the artifacts we sampled from the Jimmy Owens Site had comparable isotopic ratios, but because we did not sample any copper sheet from this locale, there is little basis for a direct comparison.

The six remaining objects tested consist of lead shot or projectiles from both the Jimmy Owens Site and Piedras Marcadas Pueblo. None of these objects have a lead isotopic composition that is similar to that of any objects from the other site or to any object that might be considered diagnostic of the expedition.

5. Discussion
The central assumption of this study is that the Coronado expedition left archaeological traces of its presence at both Piedras Marcadas Pueblo and the Jimmy Owens Site. Based on this assumption, we hypothesize that if the expedition left behind metallic armaments at both sites, these objects should have similar isotopic ratios at both locales. Copper crossbow boltheads, artifacts widely considered diagnostic of the expedition, have similar isotopic ratios at both the Jimmy Owens Site and Piedras Marcadas Pueblo, a result that is consistent with this hypothesis. Furthermore, the isotopic ratios of the majority of lead objects analyzed from Piedras Marcadas Pueblo overlap with 5 of the 7 lead objects tested from the Jimmy Owens Site. We contend the simplest explanation for the correspondence between the isotopic signatures of the lead artifacts (mostly shot) found at both sites is that they were all left by the Coronado expedition. Notably, the copper crossbow boltheads and lead objects we attribute to the Coronado expedition are also similar in isotopic composition to one another. This result further supports the interpretation that the lead artifacts are associated with the expedition and may indicate the sources of lead and copper are geologically related.

The documentary evidence does not directly indicate the geological source(s) of the expedition’s supply of lead and copper metal. The lead isotopic ratios of the artifacts we attribute to the Coronado expedition fall well within the range of values reported for lead and copper ores in Mexico (Fig. 3; Cumming et al., 1979; Hosler and MacFarlane, 1996), but are distinct from most of the values reported for Iberian ore deposits (Arribas and Tosdal, 1994; Klein et al., 2009; Marcoux, 1998; Pomiès et al., 1998; Santos-Zalduegui et al., 2004; Stos-Gale et al., 1995; Velasco et al., 1996). However, the lead
isotopic ratios of some copper ores from the Sierra Morena (Klein et al., 2009) overlap with the signatures of the crossbow boltheads measured in this study, and lead ores from the Betic Cordillera (Arribas and Tosdal, 1994; Stos-Gale et al., 1995) also have similar (although not overlapping) values to the lead objects we propose belonged to the Coronado expedition. Thus, on isotopic grounds, neither Mexico nor Spain can be excluded as the source of these objects. Although we cannot definitively identify the geologic provenance of these objects using lead isotopic measurements, we favor the interpretation they were made of metal derived from Mexican ores.

Copper metallurgy had been practiced in West Mexico for more than 800 years prior to the arrival of the Spanish (Barrett, 1987; Hosler, 2009; Hosler and MacFarlane, 1996). In Late Postclassic Mesoamerica, copper extraction and production was centered within the Tarascan empire, which covered most of the present-day state of Michoacan (Maldonado, 2008; Maldonado and Rehren, 2009). The knowledge and skill of indigenous metal workers in this region was immediately recognized by the Spanish, and Hernán Cortés used indigenous copper smiths to produce crossbow boltheads almost two decades prior to the Coronado expedition (Gagné, 2003; Rhodes, 1997). In 1533, the Spanish assumed control over the Tarascan copper industry, although they largely left the technological and structural aspects of copper production in indigenous hands (Maldonado, 2008; Thomas, 2008). It is thus relevant to note that the isotopic ratios of the crossbow boltheads reported here fall within the range of those reported for copper ores in Michoacan, although they overlap with those of copper ores from other parts of West Mexico as well (Hosler and MacFarlane, 1996). The conclusion that the copper
crossbow boltheads used by the Coronado expedition were manufactured in New Spain (as opposed to being imported from Europe), is reinforced by the observation that quarrels found in archaeological sites linked to the contemporaneous Hernando de Soto entrada in the southeastern U.S. are made of iron, not copper (Rhodes, 1997; also see Waselkov, 2010; Ewan and Hann, 1998; Smith et al., 1998). All of these lines of evidence combine to provide compelling support for the conclusion that crossbow boltheads utilized by the Coronado expedition were manufactured from copper mined in Mexico.

Although little is known about lead mining and production during the colonial period in Mexico, lead is a common byproduct of silver mining, which was well underway by the 1530’s (West, 1994). At this time, the most productive silver mines in New Spain were located in the “Provincia de la Plata” a few tens of kilometers southwest of Mexico City (West, 1994). This area broadly encompasses the five mining centers of Sulpatec, Amatepec, Taxco, Zacualpan, and Temascaltepec, and is host to both near-surface silver oxides and, at depth, argentiferous lead sulfide ores (West, 1994). In addition to the common co-occurrence of lead and silver-bearing ores, lead was also an important flux used to extract and refine silver from both oxide and sulfide ores, and was particularly crucial before the invention of the patio process in the 1550’s (West, 1994; Schooler, 2009). By 1539, at least one report indicates that miners in Taxco needed large quantities of litharge (lead oxide) to refine silver, and lead metal was in great demand (West, 1994). As lead may have been a byproduct of the silver mining operations at the Provincia de la Plata, it is intriguing to note that the lead isotopic fingerprint we have
defined for the Coronado expedition’s lead supply overlaps with that of galena (lead sulfide) samples from mines in this region, particularly in the Taxco area (Cumming et al., 1979). Thus, from a historical and geochemical point of view, the conclusion that the Coronado expedition was supplied with lead mined in Mexico appears quite plausible. There is archaeometric evidence from New World contexts that can be used to argue against the possibility the expedition was supplied with metals derived from Spanish ore. For example, fragments of galena excavated from the site of La Isabela, Dominican Republic (1494-1498) and associated with the second expedition of Christopher Columbus, have lead isotopic ratios that are consistent with a source in Spain (Thibodeau et al., 2007). The objects we attribute to the Coronado expedition do not have similar lead isotopic ratios to the lead ore from La Isabela. There are also more direct archaeometric data that support the interpretation the expedition’s lead supply was derived from Mexican ore sources. Using lead isotopes, both Joel et al. (1988) and Iñañez et al. (2010) have established that lead-based ceramic glazes were manufactured locally in Spanish Mexico during the 16th and 17th centuries. In both of these studies, the lead isotopic composition of glazes on locally produced ceramic wares differs significantly from that of glazes on wares known to have been manufactured in Spain. Furthermore, the range of isotopic ratios measured on glazes associated with both local and imported ceramics in colonial Mexico is broadly consistent with the isotopic composition of lead in Mexican and Spanish ore deposits, respectively (Iñañez et al., 2010; Joel et al., 1988). Therefore, the isotopic ratios of these lead-based glazes can be used to compare the isotopic composition of lead mined in both Mexico and Spain during the 16th and 17th centuries.
The lead isotopic ratios of objects we propose belonged to the Coronado expedition fall within the range of values reported for glazes made in Mexico, but are not similar to isotopic ratios of glazes on imported ceramics (Fig. 5). Thus, archaeometric, geochemical, and historical evidence can all be combined to support a Mexican origin for the Coronado expedition’s lead supply.

It is worth noting that the isotopic correspondence between the copper and lead objects we attribute to the Coronado expedition does not necessarily indicate the copper and lead had to be derived from the same ore deposit. We emphasize that limited isotopic variability among lead and copper ore deposits in Mexico as well as the potential for mixing of metal or ores from multiple sources does not allow us to specify the ore deposits or mining districts that were the sources of the expedition’s lead and copper. However, inferences about the geologic provenance of these objects are of secondary importance to the definition of an isotopic ‘fingerprint’ associated with the Coronado expedition’s lead and copper supply.

Due to the isotopic similarity among many of the lead artifacts from both the Jimmy Owens Site and Piedras Marcadas Pueblo, we propose these objects (which we designate with an “A” in Fig. 4) are archaeological remains of the Coronado expedition. Within this grouping we also include four copper crossbow bolt heads, artifacts considered diagnostic of the expedition’s presence. However, what of the 10 other artifacts which have lead isotopic compositions that are distinct from this group? What can be said about the origin of these artifacts and what evidence is there to support any conclusion regarding their association with the entrada?
As copper crossbow boltheads are generally considered diagnostic of the
Coronado expedition, it is quite likely that PM-607 (interpreted to be a possible crossbow
bolthead) is also an artifact from the 1540s. One important observation regarding PM-607
is that it is just a simple “cone,” likely rolled from a triangular piece of copper (Fig. 2; see
Schmader, in press). It has none of the more formal characteristics of boltheads, such as a
shaft or distinctive tip. (For a discussion of the morphology of boltheads found in Texas
and New Mexico, see Gagné, 2003; for a description of the morphology of individual
boltheads found at Piedras Marcadas Pueblo, see Schmader, in press, Table 1). In
addition to its simple construction, PM-607 is isotopically offset from the other crossbow
boltheads in this study. These observations, coupled with the fact that this bolthead is an
exact isotopic match for one of the pieces of copper sheet (PM-986; Table 1, Fig. 4), lead
us to suggest the bolthead could have been made from copper sheet on site. This
suggestion is not without precedent: copper sheet found at Pecos Pueblo may have
belonged to the Coronado expedition and could have conceivably been used in the
production of crossbow quarrels (Kidder, 1932; Rhodes, 1997). At least 32 scraps of
thick, copper or copper alloy sheets have been recovered from Piedras Marcadas Pueblo,
as well as three other boltheads with a similar conical shape to PM-607 (Schmader, in
press). The lead isotopic ratios of the three pieces of copper sheet and the one conical
bolthead measured for this study cluster together and fall within the known range of
isotopic ratios associated with copper ores from both West Mexico and Spain (Hosler and
MacFarlane, 1996; Klein et al., 2009). Although our data set is small, we suggest that
these fragments of copper sheet could also be archaeological remnants of the Coronado
expedition. If this is indeed the case, the lead isotopic signature of the copper carried by the expedition is more variable than the range of ratios measured on the other four crossbow boltheads.

The six remaining objects consist of lead shot or projectiles from both sites. Five of these artifacts have $^{206}\text{Pb}/^{204}\text{Pb}$ values greater than 19.0, $^{207}\text{Pb}/^{204}\text{Pb}$ values greater than 15.7, and $^{208}\text{Pb}/^{204}\text{Pb}$ values greater than 39.0 (Table 1; Fig. 3). Two of these artifacts are from the Jimmy Owens Site. One of these (JOS-06) was identified as a flattened 0.45 caliber bullet that dates to the late 19th century (see Section 3), and can thus be eliminated as a possible artifact of the Coronado expedition. The other artifact from the Jimmy Owens Site has a similar isotopic signature to the bullet (JOS-05), and on this basis, we suggest it is also a remnant of 19th century activity. The clear isotopic difference between the 19th century bullet and the lead shot we believe belonged to the Coronado expedition supports our position that lead isotopic analysis may be useful in distinguishing artifacts associated with Coronado from archaeological remains of later site activity.

At Piedras Marcadas Pueblo, we analyzed three 8 mm lead balls (PM-1065, PM-1087, PM-1135) and found their isotopic signatures to have the most radiogenic lead (i.e. the highest $^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb}$ values) of any of the objects analyzed for this study. The isotopic ratios of these three balls are almost identical within the precision of our measurements, an observation that leads us to conclude these objects are clearly related to one another. These three balls were part of a 20-meter line of 48 nearly identical 8 mm lead balls recovered at Piedras Marcadas Pueblo (Schmader, in press).
Although we cannot rule out the possibility these belonged to the Coronado expedition, there are several reasons to suggest they did not. Firstly, none of the lead balls analyzed from the Jimmy Owens Site have similar isotopic ratios. Secondly, the lead isotopic composition of these balls does not fall within the known range of lead ores anywhere in Mexico. Thirdly, the isotopic composition of these balls is consistent with lead ores from the Viburnum trend (Goldhaber et al., 1995), a region of lead mineralization in the central U.S. that was first worked on a large scale by the French in the early 18th century and was never actively exploited by the Spanish (Schooler, 2009).

A fourth lead ball (PM-19) sampled from Piedras Marcadas Pueblo has an isotopic signature that is much less radiogenic than any of the artifacts in this study, and is consistent with a geologic origin in Spain (compare to Santos-Zalduegui et al., 2004). Because many of the expedition’s members may have brought their own supplies, it is plausible that this artifact did originate with the Coronado expedition. However, this artifact may also be associated with later Spanish activity, or may be a modern object. Although lead isotopic ratios constrain the geologic provenance of these four pieces of lead shot, determining the likelihood that they are 16th century, 20th century, or derive from a time-period in between is beyond the scope of this study.

6. A case study: Calabacillas Pueblo

As an exploratory application of the method developed and described in this paper, we have measured the lead isotopic composition of a single fragment of copper-based scrap found on the surface of Calabacillas Pueblo in New Mexico (New Mexico Laboratory of Anthropology site number 289, see Table 1). 2.4 miles north of Piedras
Marcadas, Calabacillas was also one of the Tiguex pueblos in the middle Rio Grande Valley that was occupied at the time of European contact (Barrett, 2002; Schmader, in press). In some reconstructions of the Coronado expedition’s interactions with pueblos along the middle Rio Grande Valley, Calabacillas is considered to be one of the pueblos visited by the expedition and described in its documentary sources (Barrett, 2002; Schmader, in press).

The analyzed scrap of copper was collected from the surface of the site, and is visually and physically similar to copper scraps recovered from Piedras Marcadas Pueblo. There are no external characteristics or contextual information that would allow us to determine if it is a modern object or the remnant of 16th, 17th, 18th or 19th century activity. The sample was prepared and analyzed according to the same protocol described in Section 3. The lead isotopic composition of the scrap falls very close to the isotopic ratios of copper sheet we analyzed from Piedras Marcadas Pueblo (Table 1, Figs. 3 and 4). Although we caution against overinterpretation of a single, surface artifact (see Section 7 for additional caveats), it is a tantalizing result and a potentially useful application of the method described in this paper. If the copper sheet measured from Piedras Marcadas Pueblo is indeed mid-16th century, then this piece of copper scrap has a lead isotopic composition that is consistent with the range of ratios we would expect from an artifact left by the Coronado expedition.

7. Implications for future studies

We thus propose that the very narrow range of isotopic ratios for the copper crossbow boltheads and for much of the lead shot from both sites (1) strengthens
arguments for the presence of the Coronado expedition at Piedras Marcadas Pueblo and the Jimmy Owens Site, and (2) suggests that a significant portion of the lead and copper armaments carried by the expedition are likely to have similar or identical lead isotopic ratios. Notably, the fragments of lead we attribute to the expedition have a more constrained range of lead isotopic ratios than the copper artifacts, suggesting lead metal has the most specific isotopic fingerprint. The lead isotopic ratios of the metallic lead objects we attribute to the Coronado expedition range between 18.738 and 18.833 for \( \frac{^{206}\text{Pb}}{^{204}\text{Pb}} \), 15.651-15.670 for \( \frac{^{207}\text{Pb}}{^{204}\text{Pb}} \), and 38.716-38.776 for \( \frac{^{208}\text{Pb}}{^{204}\text{Pb}} \). The isotopic ratios of the four crossbow boltheads measured in this study are 18.670-18.750 for \( \frac{^{206}\text{Pb}}{^{204}\text{Pb}} \), 15.652-15.654 for \( \frac{^{207}\text{Pb}}{^{204}\text{Pb}} \), and 38.611-38.700 for \( \frac{^{208}\text{Pb}}{^{204}\text{Pb}} \). However, since it is possible that fragments of copper sheet (and PM-607) from Piedras Marcadas Pueblo may also represent evidence of the Coronado expedition, the range of values associated with the expedition’s copper may be larger. Nevertheless, this fingerprint has the potential to help identify other archaeological remnants of the expedition and therefore aid in the future identification of archaeological sites tied to the Coronado entrada.

Although the results of this study support our hypothesis that lead and copper armaments used by the Coronado expedition have a characteristic range of lead isotopic ratios, we caution against making the assumption that this signature is uniquely connected with the Coronado entrada. The results of Cumming et al. (1979) indicate that there is only modest variability in the isotopic composition of galena from mineral deposits across West and Central Mexico. Furthermore, the data in Hosler and
MacFarlane (1996) indicate there is some overlap between the lead isotopic signatures of copper minerals from different regions in West Mexico. We do not, at this time, have enough data (ours or from the literature) regarding the lead isotopic composition of metals carried by later 16th & 17th century Spanish expeditions and settlers to know how they compare to the objects analyzed in this study. However, it is encouraging to note that the vast majority of lead isotopic ratios reported for lead-based glazes on ceramics produced in colonial Mexico have lead isotopic compositions that are similar to, but analytically distinct from our proposed fingerprint (Fig. 5). Additionally, the lead isotopic composition of Spanish bullets that derive from Mexican ores in 17th century missions in Texas and Oklahoma have a much greater range than our proposed fingerprint (Schooler, 2009). This isotopic spread likely reflects the great expansion of Spanish lead and silver mining in the 16th and 17th centuries (see Schooler, 2009 for a review). However, several mines in the vicinity of Mexico City continued to produce lead throughout Mexico’s colonial period (West, 1994). Thus, it is possible that the mines that supplied the Coronado expedition may have continued to supply at least some lead ore to the Spanish over the course of the whole colonial period.

Further complicating matters, the lead isotopic ratios of ores in central New Mexico (especially those of the Cerrillos Hills) are similar to those of West Mexican ores (e.g. compare Habicht-Mauche et al., 2000 and Habicht-Mauche et al., 2002 to Hosler and MacFarlane, 1996). It is however quite certain that neither copper nor metallic lead was being produced from these ores at the time of the Coronado expedition (Thomas, 2008; Ramenofsky et al., 2008). One of the earliest known smelting sites in the U.S.
Southwest is the 17th century metallurgical facility at Pa’ako Pueblo, north of Albuquerque, New Mexico. At Pa’ako Pueblo, the lead isotopic ratios measured on copper sheet of apparently local production overlap with those of the copper sheet we sampled from Piedras Marcadas Pueblo, and with the single piece of copper scrap from Calabacillas Pueblo (Thomas, 2008; Thomas and Thibodeau, 2010). These results suggest that some of the copper produced in 17th century New Mexico may overlap with our “Coronado fingerprint.” Characterizing the range of isotopic signatures of Colonial period (1598-1821) metals in the Southwest should be an important component of future research.

As we caution that our proposed fingerprint may not be unique, we must also acknowledge it may not be a comprehensive characterization of the lead and copper armaments used by the expedition. The piece of shot with a Spanish isotopic signature is illustrative of the possibility that there may be a wider range of isotopic ratios associated with the expedition’s metallic weaponry. Until there are additional isotopic data on lead shot, copper sheet, and copper crossbow boltheads from other archaeological sites in the Southwest that can be linked with the entrada, it is difficult to evaluate this possibility. These caveats preclude using lead isotopes as the sole line of evidence when attempting to link archaeological sites to the Coronado expedition. However, although lead isotopic analysis of metals is not, by itself, sufficient to definitively identify archaeological evidence of Vázquez de Coronado’s entrada, when used in conjunction with other lines of evidence, it may be a useful tool that could help bolster or refute claims of the expedition’s presence in particular archaeological sites. The narrow range of isotopic
ratios shared by lead artifacts and copper crossbow boltheads from both Piedras Marcadas Pueblo and the Jimmy Owens Site suggests that sites associated with the expedition should have artifacts with nearly identical lead isotopic compositions. For example, all the lead objects we have linked to the Coronado expedition have an average $^{207}\text{Pb}/^{204}\text{Pb}$ ratio of 15.657 (with a standard deviation of 0.006). This spread is just slightly larger than the 2s external error associated with the measurement of $^{207}\text{Pb}/^{204}\text{Pb}$. Although the spread of $^{208}\text{Pb}/^{204}\text{Pb}$ and $^{206}\text{Pb}/^{204}\text{Pb}$ ratios in these same objects is greater, this discrepancy is accounted for by the fact that the relative abundances of $^{208}\text{Pb}$ and $^{206}\text{Pb}$ are geologically more variable than that of $^{207}\text{Pb}$. The specificity of our proposed isotopic fingerprint emphasizes the necessity of applying high-precision analyses to this problem, and for ensuring the inter-lab comparability of lead isotopic measurements.

8. Conclusion

We conclude that lead shot, copper crossbow boltheads, and copper sheet associated with the Coronado expedition have a specific isotopic fingerprint, and propose this fingerprint can be used in the future to help identify material culture associated with the expedition at other archaeological sites in Sonora, Arizona, New Mexico, Texas, and Kansas. Moreover, the isotopic signature of these objects is consistent with the conclusion that most of the expedition’s supply of lead and copper was produced from Mexican ores. Future work could expand upon our results in two ways. The analysis of additional artifacts from Piedras Marcadas Pueblo, the Jimmy Owens Site, or other archaeological sites linked to the Coronado expedition would either substantiate or expand upon our proposed fingerprint. We emphasize, however, that any reliable ‘fingerprint’ must either
be characterized using diagnostic artifacts (like crossbow bolheads) or derive from the comparison of lead isotopic data on similar artifacts from multiple sites. Alternatively, applying lead isotopic analysis to metals unassociated with the Coronado expedition would foster a better understanding of the differences or similarities between the lead isotopic composition of artifacts from the 1540’s, and those that are the result of later activity. The results of this study demonstrate the utility of lead isotopes in addressing archaeological problems that go beyond the determination of provenance, and their potential to help illuminate the movements of the 1540 to 1542 expedition of Vázquez de Coronado in the U.S. Southwest.

Acknowledgments

This project was initiated by Charles Haecker (National Park Service-Heritage Partnerships program) and developed in collaboration with Charles Haecker, Clay Mathers (The Coronado Institute) and Matt Schmader (Open Space Division, City of Albuquerque). This research was supported by NSF grant BCS-0852270, which also provided funding to A.M. Thibodeau. This project was also funded, in part, by a grant from the National Park Service-Intermountain Region to Charles Haecker and a grant from the state of New Mexico (sponsored by District 13 Senator Dede Feldmen). The results of the pilot study for this project were reported by Charles Haecker in the paper “Tracing Coronado’s Route through Trace Element Analysis” at the 2008 Society for Historical Archaeology (SHA) Conference in Albuquerque, New Mexico. Access to samples from the Jimmy Owens Site was graciously provided by Nancy Marble and the
staff at the Floyd County Museum in Floydada, Texas. Access to samples from Piedras Marcadas Pueblo was provided by Matthew Schmader and the City of Albuquerque. T.J. Ferguson, Charles Haecker, David J. Killick, and Matt Schmader all commented upon and greatly improved the final content of this paper. Mark Baker provided invaluable assistance in the lab.

References


Blakeslee, D.J., Flint, R., Hughes, J.T., 1997. Una barranca grande: recent archaeological evidence and a discussion of its place in the Coronado route. In:


Damp, J., 2005. The Battle of Hawikku, Archaeological Investigations of the Zuni-Coronado Encounter at Hawikku, the Ensuing Battle, and the Aftermath


Flint, R.F., Flint, S.C., 2005. Documents of the Coronado Expedition, 1539e1542: “they were not familiar with His Majesty, nor did they wish to be his Subjects.” Southern Methodist University Press, Dallas.


Archaeological Annual Conference.


Schmader, M.F., 2008a. Nailing down Coronado: assemblage and tactics of a 16th


Table 1. Lead Isotopic Ratios of Artifacts from the Jimmy Owens Site and Piedras Marcadas Pueblo

<table>
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<tr>
<th>Artifact ID</th>
<th>Artifact Description</th>
<th>$^{208}\text{Pb}/^{206}\text{Pb}$</th>
<th>$^{207}\text{Pb}/^{206}\text{Pb}$</th>
<th>$^{206}\text{Pb}/^{204}\text{Pb}$</th>
<th>$^{207}\text{Pb}/^{204}\text{Pb}$</th>
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<td>Piedras Marcadas (LA-290)$^a$</td>
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<tr>
<td>PM-35</td>
<td>crossbow bolthead</td>
<td>2.0688</td>
<td>0.83837</td>
<td>18.670</td>
<td>15.652</td>
<td>38.625</td>
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<td>PM-607</td>
<td>crossbow bolthead</td>
<td>2.0862</td>
<td>0.84804</td>
<td>18.417</td>
<td>15.619</td>
<td>38.421</td>
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<td>PM-865</td>
<td>crossbow bolthead</td>
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<td>0.83704</td>
<td>18.700</td>
<td>15.653</td>
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<td>copper sheet</td>
<td>2.0862</td>
<td>0.84811</td>
<td>18.423</td>
<td>15.625</td>
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<tr>
<td>PM-546</td>
<td>copper sheet</td>
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<td>0.83653</td>
<td>18.672</td>
<td>15.620</td>
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<td>PM-716</td>
<td>copper sheet</td>
<td>2.0677</td>
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<td>18.607</td>
<td>15.612</td>
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<td>PM-716c</td>
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<td>C-1</td>
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<td>0.83498</td>
<td>18.709</td>
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<td>38.570</td>
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</tr>
<tr>
<td>R, repeat measurement</td>
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</table>

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<thead>
<tr>
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<td>JOS-10b crossbow bolthead</td>
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<tr>
<td>JOS-10a crossbow bolthead with some corrosion</td>
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</tr>
<tr>
<td>JOS-31b crossbow bolthead</td>
<td></td>
</tr>
<tr>
<td>JOS-31a crossbow bolthead with some corrosion</td>
<td></td>
</tr>
<tr>
<td>JOS-01 lead ball</td>
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<tr>
<td>JOS-02 lead ball</td>
<td></td>
</tr>
<tr>
<td>JOS-03 lead ball</td>
<td></td>
</tr>
<tr>
<td>JOS-04 lead sprue</td>
<td></td>
</tr>
<tr>
<td>JOS-05 melted lead</td>
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<td>JOS-06 flattened lead piece</td>
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<tr>
<td>JOS-07 lead ball</td>
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|  |  |  |  |  |
|---|---|---|---|
| JOS-10b | 2.0640 | 0.83473 | 18.750 | 15.652 | 38.700 |
| JOS-10a | 2.0628 | 0.83415 | 18.762 | 15.650 | 38.702 |
| JOS-31b | 2.0637 | 0.83623 | 18.721 | 15.654 | 38.633 |
| JOS-31a | 2.0642 | 0.83630 | 18.723 | 15.659 | 38.649 |
| JOS-01 | 2.0655 | 0.83486 | 18.754 | 15.656 | 38.736 |
| JOS-02 | 2.0653 | 0.83485 | 18.753 | 15.656 | 38.730 |
| JOS-03 | 2.0654 | 0.83486 | 18.754 | 15.657 | 38.732 |
| JOS-04 | 2.0673 | 0.83546 | 18.739 | 15.656 | 38.742 |
| JOS-05 | 1.9726 | 0.79373 | 19.888 | 15.786 | 39.230 |
| JOS-06 | 2.0352 | 0.81830 | 19.200 | 15.712 | 39.075 |
| JOS-07 | 2.0669 | 0.83535 | 18.739 | 15.654 | 38.732 |

*aArtifacts curated by the City of Albuquerque, Open Space Division*  
*bArtifacts curated by the Floyd Country Historical Museum (Floydada, TX)*  
*cR, repeat measurement*
Figure 1. Approximate locations of Piedras Marcadas Pueblo and the Jimmy Owens Site.
Figure 2. Copper sheet (PM-986) and a possible “conical” copper crossbow bolt head (PM-607) from Piedras Marcadas Pueblo that have analytically indistinguishable lead isotopic ratios. A spot where copper metal was drilled can be seen in the bottom left portion of the copper sheet (PM-986). (Photo credit: Matthew Schmader).
Figure 3. Lead isotopic ratios of all artifacts analyzed from Piedras Marcadas Pueblo and the Jimmy Owens Site. Dashed outlines indicate the range of lead isotopic ratios measured on galena from ore deposits in Mexico (taken from Cumming et al., 1979). Note that all artifacts attributed to the Coronado expedition fall within this range. The boxed areas indicate the regions covered by the graphs in Fig. 4. All symbols are smaller than the 2s external errors associated with the measurements.
Figure 4. Lead isotopic ratios of artifacts that may be associated with the Coronado expedition. The letter A is used to denote a group of lead artifacts (n=12) and copper crossbow bolheads (n=4) from Piedras Marcadas Pueblo and the Jimmy Owens Site that have very similar isotopic ratios. Copper sheet from Piedras Marcadas Pueblo and Calabacillas Pueblo plot apart from this grouping, along with an artifact considered to be a possible crossbow bolhead (PM-607).
Figure 5. Comparison between the lead isotopic ratios of lead objects from this study and those of lead-based glazes on 16th and 17th century majolica, Romita, and plain-glazed ceramics excavated from archaeological sites across New Spain (from Joel et al., 1988; Iñañez et al., 2010). The data points plotted include only lead objects from the Jimmy Owens Site and Piedras Marcadas Pueblo that we attribute to the Coronado expedition. Objects from Piedras Marcadas Pueblo and the Jimmy Owens Site have lead isotopic ratios that overlap with those of lead-based glazes on ceramics manufactured in Mexico. The fields for the lead-based glazes are drawn to encompass the errors reported with the isotopic measurements and are meant to aid the visual comparison of existing data with the data we report. Except where shown, the symbols that represent objects from Piedras Marcadas Pueblo and the Jimmy Owens Site are larger than the 2s external errors associated with the measurements.
APPENDIX B: AN ALTERNATIVE APPROACH TO THE PREHISPANIC TURQUOISE TRADE

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AN ALTERNATIVE APPROACH TO THE PREHISPANIC TURQUOISE TRADE

by

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\textsuperscript{3}Arizona State Museum

Introduction

The major turquoise deposits of North America are concentrated within the southwestern United States across Arizona, New Mexico, Colorado, Nevada and southern California, and in northern Mexico in the state of Sonora (Fig. 1). Turquoise is a blue-green hydrated copper aluminium phosphate (\(\text{CuAl}_6(\text{PO}_4)_4(\text{OH})_8\cdot 4\text{H}_2\text{O}\)) that was both highly valued and widely exchanged among many prehispanic societies in the American Southwest and Mexico. In the Southwest, turquoise was fashioned into a wide variety of forms, including beads and pendants, as well as nose and lip plugs. It was also used to construct elaborate inlays, as a part of intricate mosaic designs, and carved into zoomorphic forms (Snow 1973; Jernigan 1978). Turquoise appears most frequently in the archaeological record of the Southwest after \(\sim\) AD 900 (Snow 1973; Windes 1992), and large quantities have long been associated with great house and small house sites in Chaco Canyon, New Mexico (Windes 1992; Mathien 2001). Turquoise was also used in
Mesoamerica, thousands of kilometres away from the well-known mines scattered across the present-day American Southwest and northern Mexico. In Mesoamerica, blue-green stones, particularly jade, were highly valued and widely circulated for thousands of years prior to the arrival of the Spanish. Although turquoise is reported to have been found in isolated instances in Mesoamerica as early as the Formative Period (e.g. Vaillant 1935), its most widespread use was during the Postclassic (AD 900–1521), when it was employed by the Mixteca and the Mexica to create elaborate mosaics and other ceremonial and status objects (e.g. McEwan et al. 2006; Saville 1922). Because there is little evidence of turquoise mining in Mesoamerica, many southwestern and Mesoamerican archaeologists believe that turquoise may have been acquired through trade with the American Southwest, an idea that has sparked an enduring debate (e.g. Kelley and Kelley 1975; Weigand et al. 1977; Lister 1978; McGuire 1980; Frisbie 1983; McGuire 1993; Wilcox 1986; Doyel 1991; Weigand and Harbottle 1993; Harbottle and Weigand 1992; Weigand 1994).

Since the 1970s, both archaeologists and physical scientists have sought to reconstruct the prehispanic turquoise trade by developing methods to identify the geologic provenance of turquoise recovered from the archaeological record or associated with ancient objects. Because of its long history of use in much of the prehispanic American Southwest and Mexico, turquoise presents a significant opportunity to address questions of resource procurement and exchange across a wide range of societies and at an array of spatial and temporal scales. However, turquoise has proved to be a difficult mineral to trace and efforts to do so have encountered a variety of the archaeological,
geological, and chemical complexities associated with the problem. Lead and strontium isotopes may offer new answers to longstanding questions about the prehispanic turquoise trade. In the present study, lead and strontium isotopic measurements are used to link turquoise from an archaeological site in the Tucson Basin to prehispanic turquoise mines in the Silver Bell Mountains of southern Arizona. The positive results of this case study illustrate the potential of these two geochemical tracers to overcome the problems identified by previous researchers, and provide a tool that can link turquoise from site to source.

Prehispanic turquoise mines in the American Southwest and Mexico

Since the mid-nineteenth century, ideas about prehispanic turquoise mining and exchange have abounded in both the scientific and popular imagination. Geologist William Blake was the first to formally comment on the grand scale of the prehispanic turquoise mines found near Cerrillos, New Mexico. In an article for the American Journal of Science, Blake (1858: 227) states, ‘On reaching the locality I was struck with astonishment at the extent of the excavation … [i]t is an immense pit … and tens of thousands of tons of rock have been broken out.’ Blake was describing the great pit on the western side of Mount Chalchihuitl in the Cerrillos Hills Mining District, now the most famous locale associated with prehispanic turquoise mining in North America. Situated some 20 km southwest of present-day Santa Fe, New Mexico, the district has a history of mining that spans the past 1,000 years or more (Mathien 1998). Mined initially for turquoise and later for lead ores by Ancestral Puebloan groups (Schroeder 1979; Warren and Weber 1979; Bice et al. 2003), the Cerrillos Hills also contain ores of copper,
zinc, gold and silver that were later worked by both Spanish and American miners (Disbrow and Stoll 1957; Mathien 1998). In 1915, Joseph Pogue, a geologist with the National Academy of Sciences, published an exhaustive monograph on turquoise, which included a compilation of the known turquoise deposits across the world (Pogue 1974). Despite his knowledge of other ancient turquoise mines in the American Southwest, the immensity of the prehispanic workings in the Cerrillos Hills Mining District led him to declare, ‘this deposit must have supplied much of the turquoise which was so widely used in pre-Spanish times, not only in the Southwest, but in Mexico as well, for no other sources are now known at all adequate to account for the quantities employed’ (1974: 52).

In the decades that followed Blake’s original description of the Cerrillos Hills mines, many prehispanic turquoise workings from across the American Southwest were rediscovered and described by prospectors, journalists and geologists (Bennett 1970). In New Mexico, Snow (1891) reported on the ancient workings of the Burro Mountains, and Hidden (1893) reported the presence of prehistoric mines near the town of Hatchita (in the Little Hatchet Mountains), as well as in the Jarrilla Mountains (Fig. 1). The discovery of hundreds of additional prehispanic turquoise workings broadened perspectives on the scope and scale of turquoise mining in the prehispanic American Southwest, leaving many with the impression that ‘very few turquoise mines have ever been found that did not show some evidence of having been previously mined by Indians’ (Bennett 1970: 35).

Consequently, it has been speculated that many of the major deposits of turquoise
in the American Southwest were the source of turquoise used by Mesoamerican groups in prehistory. On 3 June 1895, the *Tombstone Prospector* commented on the prehistoric turquoise mines in the Dragoon Mountains of southeastern Arizona, stating, ‘Even centuries ago the value of this stone was apparent among the extinct races, as there is evidence of extensive workings at Turquois by the Aztecs who are supposed to have inhabited this entire section of the country after this precious mineral.’ On 18 March 1898, a headline in the *San Francisco Call* announced, ‘Long Lost Mines of Precious Gems are Found Again, Located in the Remotest Wilds of San Bernardino Country and Marked by Strange Hieroglyphics’ regarding the turquoise mines of the Halloran Hills in California’s eastern Mojave Desert. The accompanying text, which introduces an article by explorer Gustav Eisen (1898), states, ‘[t]here have been found the mines of the ancients, long lost to knowledge and so the secret source from which the Aztecs drew their supply of turquoise is no longer a secret locked in the mists of the past’. Although there is no evidence that any Mesoamerican group ever mined turquoise in the American Southwest, these early ideas about the source of the turquoise used in Mesoamerica still reverberate in present-day archaeological discussions of long-distance trade.

In spite of the likely importance of turquoise in local, regional and long-distance exchange networks, there has been little direct study of prehispanic mines in the American Southwest or Mexico. Formal archaeological investigation of the tools, ceramics, shelters or workshops found at or near known mining sites is rare (for examples of such studies see: Leonard and Drover 1980; Warren and Mathien 1985; Wiseman and Darling 1986). A number of factors have converged to make the archaeological study of
turquoise mines difficult, and in some cases, impossible. Because turquoise in the American Southwest often occurs near economically significant deposits of copper, molybdenum, lead and silver, historic and modern mining practices have encroached upon, or sometimes completely obliterated sites of ancient mining. In New Mexico, ancient workings in the Burro Mountains have been destroyed by the expansion of open pit copper mines. Ancient turquoise mining sites on Ithaca Peak in the Cerbat Mountains and in the Silver Bell Mining District (both in Arizona) have met a similar fate. Even in the famous Cerrillos Hills Mining District, which contains some of the best-preserved and studied prehispanic mines in North America, centuries of mining and artefact collection had already compromised the integrity of the archaeological remains before archaeological surveys began (Warren and Mathien 1985). Additionally, much of the literature surrounding ancient turquoise mines is vague, cannot be verified, and does not provide specific location information. As Bennett (1970: 35) notes, ‘[a] singular lack of imagination was used in naming the hills or ridges or mountains on which the mines were situated. Turquoise Ridges; Turquoise Mountains; Turquoise Hills; and Castle Dome Ridges, Mountains, and Hills are scattered all over several states.’

Understanding the exchange of turquoise between American southwestern and Mesoamerican societies becomes even more difficult in light of the paucity of information available regarding turquoise sources closer to major population centres of Mesoamerica. For example, hypotheses regarding the trade of turquoise from the American Southwest to Mesoamerica imply that major turquoise deposits did not exist in Mesoamerica, or if they did, were either not known to or not mined by Mesoamerican
groups. To accurately evaluate such hypotheses it is necessary to consider the evidence for turquoise deposits closer to the core areas of Mesoamerican civilisations that utilised the stone. The geologic literature documents turquoise in several localities in Baja California Norte, in association with areas of major copper mineralization in Sonora, and at several localities in Zacatecas (Panczer 1987: 382–383). Weigand (1994: 31) reports evidence of prehistoric workings in at least five areas in Sonora and two areas in Zacatecas, as well as in Chihuahua, Coahuila, and San Luís Potosí. In addition to mines in Sonora and Zacatecas, Di Peso (1974: 277) provides references attesting to the existence of turquoise sources in Coahuila and Chihuahua and to deposits of chrysocolla and turquoise in Jalisco. He also indicates that there are small surface outcrops of turquoise from Guerrero and Aguascalientes (Di Peso 1974: 207). However, the references do not disclose their sources of information about these occurrences.

Furthermore, there have also been reports of turquoise from Veracruz, Tehuantepec (Michoacan), and Chiapas (Mathien 1981a: 178, citing Sigleo). However, the lack of available information about the locations of these turquoise sources, the common confusion of turquoise with other blue-green minerals, and conflicting information between geological and archaeological reports makes it difficult to verify many of these claims, particularly for the reported mines in central and southern Mexico. Sinkankas (1976: 143–144) makes the illuminating observation that in the Concepción del Oro area of Zacatecas, the mineral prosopite (CaAl₂(F,OH)₈) is often mistaken for turquoise.

**Past approaches to tracing turquoise**

To better understand ancient turquoise mining and trade, many researchers have
utilised geochemical methods to investigate the source of turquoise artefacts. The majority of these studies approach the problem from a compositional perspective and use trace and major element concentrations to draw links between turquoise objects and known mines (Sigleo 1975; Weigand et al. 1977; Mathien 1981b; Harbottle and Weigand 1992; Mathien and Olinger 1992; Weigand 1994; Kim et al. 2003). Early applications of trace and major element measurements were partially driven by the ready availability and low cost of analytical methods such as neutron activation analysis (NAA) and X-ray fluorescence (XRF), which allowed large numbers of samples to be analysed. Although these efforts to address questions of turquoise provenance have made important contributions to the topic, published data from compositional studies have not been able to define unique or characteristic signatures for the many mines in the American Southwest. However, new approaches to turquoise provenance are now being explored, including the use of copper and hydrogen isotopes (Hull et al. 2008) and lead and strontium isotopes (Thibodeau et al. 2007b; this study).

The geology and mineralogy of turquoise

The difficulty of using elemental concentrations to trace turquoise can be explained by the mineralogical characteristics of turquoise and the circumstances of its formation. Turquoise comes in a variety of colours, from the familiar ‘robin’s egg’ blue, to apple green. It was once commonly believed that visual inspection was sufficient to identify the source of a piece of turquoise. Although some claim that high-grade turquoise may have distinctive types of matrix that could help narrow the field of possible sources (Arrowsmith 1974), appearance cannot be reliably applied to determine geologic
provenance, particularly of archaeological samples. In his description of turquoise at Mount Chalchihuitl, Blake (1858: 229) observed, ‘various shades of apple-green and pea-green, passing into bluish green … some fragments having a blue color were found’. He went on to note:

On breaking open one of the dark green fragments a small cavity was found at the center … the color gradually shading into white. There are not any distinct layers … but the color gradually diminishes from the surface to the center. A variation in the different amount of coloring matter in different specimens according to the circumstances of formation is thus indicated, it is seen that the composition of the mineral cannot be regarded as constant.

These early observations accurately note a common characteristic of turquoise: its variable composition, even on the scale of a single nodule or vein. Ideally, turquoise has the formula $\text{CuAl}_6(\text{PO}_4)_4(\text{OH})_8\cdot4\text{H}_2\text{O}$ and crystallises with triclinic symmetry (Cid-Dresdner 1965; Foord and Taggart 1998). However, high purity crystalline turquoise is rare (Braithwaite 1981; Foord and Taggart, 1998; Barwood 2003). Instead it is usually cryptocrystalline or massive, incorporates many impurities, and may have a wide variety of compositional and visual characteristics.

Turquoise is classified by mineralogists as one of the six known minerals within the ‘turquoise group’ (Foord and Taggart 1998). The other five minerals, listed in Table 1, are similar to turquoise, and differ primarily due to substitution of other cations (positively charged ions) for $\text{Cu}^{2+}$ or $\text{Al}^{3+}$. Many minerals within the turquoise group are known to form partial or complete solid solution series with one another, a phenomenon that can greatly impact the composition of a given sample. For example, an extensive
solid solution series exists between the turquoise and chalcosiderite end members. Minerals that lie along this series may have various proportions of \( \text{Al}^{3+} \) to \( \text{Fe}^{3+} \), which result in a wide range of blue to green colouration in samples of ‘turquoise’. Even more notable is the complete solid solution series between turquoise and planerite, which is a light blue to blue-green copper-deficient analogue to turquoise. Foord and Taggart (1998) suggest that most samples described as ‘turquoise’ in the literature may be closer in composition to planerite. The recognition that turquoise, as popularly defined, is actually a group of minerals with widely variable compositions is consistent with the wide array of colours observed in ‘turquoise’ from the same deposit, outcrop or even hand sample. The prehispanic cultures of the American Southwest and Mexico embraced these variations and used ‘turquoise’ of all colours and quality. In many of the famous Mixtec pieces, the artists used differences in the colour of various mosaic pieces to achieve specific design features (McEwan et al. 2006). However, these same variations have hindered the use of elemental concentrations to fingerprint mines and identify the source of turquoise.

The variable nature of turquoise can be explained through consideration of the processes that create it. Turquoise forms in the weathering environment, via the interaction of meteoric waters with copper, phosphorous, and aluminium-bearing rocks. Major deposits of turquoise are confined to arid or semi-arid regions worldwide, and are known in Egypt, Iran, China, Afghanistan and the USA. In parts of the American Southwest and northern Mexico, turquoise is often found in the oxidised portions of copper porphyry deposits that are especially common across Arizona, New Mexico, and
Sonora. In the American Southwest, it is commonly found at shallow depths (30 m or less) and precipitates as veins or nodules in highly weathered and fractured felsic igneous rocks, especially monzonites, latites and trachytes. In many cases, these host rocks are inferred to have supplied the elemental and molecular constituents necessary to form turquoise; copper from disseminated copper-bearing minerals (e.g. chalcopyrite), phosphorous from apatite, and aluminium from feldspars, clays (especially kaolinite) or other aluminium-rich phases (Paige 1912; Pogue 1974; Pearl 1941).

However, turquoise is not limited to forming from the weathering of igneous rocks. Turquoise deposits on the Sinai peninsula in Egypt are found in sedimentary rocks where copper and phosphorous-charged ground waters interacted with aluminium-rich concretions made of alunite and gibbsite (Hussein et al. 1994–1995). In the American Southwest, turquoise can be found within weathered aluminium-bearing sedimentary rocks in many locales, including the Canyon Creek mine (Moore 1968; Welch and Triadan 1991), the Dragoon Mountains (Crawford and Johnson 1937), the Jarrilla Mountains (Crook 2002), and at numerous deposits in central and northern Nevada (Morrissey 1968). The source of copper and phosphorous in these deposits may lie in adjacent igneous rocks (which sometimes also contain turquoise), or within the sedimentary rocks that host the turquoise. A detailed study examining the genesis of turquoise mineralisation in the Jarilla Mountains reveals that turquoise hosted by shale deposits derived phosphate from layers of shale that are rich in apatite and xenotime (Crook 2002). Notably, turquoise in the Jarrilla Mountains can also be found in weathered quartzmonzonites, and, from a geochemical perspective, it is likely that
turquoise within the area has two distinct geological origins (Lueth 1998).

The weathering processes that create turquoise can produce localised and uneven effects, and thus create heterogeneities in the chemical composition of turquoise across a deposit, or within a single nodule or vein. Additionally, a chunk of turquoise, whether hit off an outcrop or made into a pendant, often contains other mineral phases. These impurities have also played a role in confounding efforts to trace archaeological turquoise. Minerals commonly associated with turquoise include (but are not limited to) quartz, pyrite, limonite, kaolinite, alunite, sericite and jarosite. The common appearance of these minerals near or within turquoise deposits is unsurprising, since most can be associated with turquoise formation. For example, pyrite is an iron-sulphide mineral that, when oxidised, acidifies meteoric water and makes it possible to leach copper and phosphate from country rock. The frequent association of iron oxides with turquoise (e.g. limonite) is testament to the role of pyrite oxidation and decomposition in the processes that form turquoise (e.g. see Paige 1912). As previously mentioned, minerals such as kaolinite, alunite and sericite are often implicated as the source of aluminium in turquoise. In several deposits that have been studied in detail, jarosite is interpreted to have formed from solutions that originally precipitated turquoise, but became depleted in phosphorous and copper (Paige 1912; Lueth 1998).

**Lead and strontium isotopes as tracers of turquoise**

*Why lead and strontium?*

High-precision lead and strontium isotope geochemistry offers a new opportunity to reconstruct turquoise procurement and exchange. Lead and strontium occur as minor
or trace elements in most rock-forming minerals, and can be found in measurable concentrations in turquoise. Both elements have four stable isotopes, but the relative abundance of these isotopes is widely variable in nature. Variation within these two isotopic systems is created by the radioactive decay of long-lived parent isotopes of rubidium (for strontium) and uranium and thorium (for lead).

Lead and strontium isotopic ratios have an established track record as powerful tracers and can be precisely and routinely measured using multi-collector-inductively coupled plasmamass spectrometry (MC-ICP-MS), and thermal ionization mass spectrometry (TIMS). In the geosciences, isotopic ratios of lead and strontium are commonly used to track the sources of pollutants and environmental contaminants (e.g. Bolhofer and Rosman 2001), to determine the source of metals found in ore deposits (e.g. Bouse et al. 1999), and to gain insight into weathering processes and water–rock interaction (e.g. Probst et al. 2000; Négrel et al. 2010). They are also used as tracers of archaeological materials, and can be employed to link metals and minerals from the archaeological record to specific ore deposits (e.g. Gale and Stos-Gale 1982; Farquhar et al. 1995; Stos-Gale et al. 1997; Thibodeau et al. 2007), and applied to teeth and bone to provide insight into human movement and migrations (e.g. Müller 2003, Price et al. 2002). Discussions of lead and strontium isotope geochemistry, and a review of their applications to both geological and archaeological questions can be found elsewhere (Faure 1986; Brothwell and Pollard 2005; Faure and Mensing 2005).

Aside from their myriad established applications, lead and strontium isotopes may also prove to be effective tracers of turquoise. Lead isotopes were first applied to
turquoise by Young et al. (1996) but they were unable to use their results to clearly differentiate among several mines in the American Southwest. However, these conclusions can now be re-evaluated with high-precision techniques that offer far greater resolution. For example, a pilot study that applied high precision lead and strontium isotopic measurements to 17 turquoise fragments from five locales found that samples from each deposit had distinct isotopic signatures (Thibodeau et al. 2007b). Unlike other tracers that have been applied to turquoise, lead and strontium isotopes are not significantly fractionated or partitioned by weathering processes, making them appropriate tracers for a mineral that forms in the weathering environment and may be altered after deposition. Furthermore, the processes that cause lead and strontium to vary in their isotopic composition are fundamentally different from those that produce variation in elemental concentrations, or those that alter the isotopic ratios of either hydrogen or copper.

Lead and strontium incorporated into turquoise should derive from the rocks or minerals that interacted with the turquoise-precipitating waters. Thus, assuming no significant in-growth of radiogenic lead and strontium after deposition, the isotopic composition of turquoise should broadly reflect the geologic context of specific deposits, and the circumstances under which the turquoise formed. As described above, turquoise can form as a weathering product of the same rocks that host the mineralisation, and many of the minerals associated with turquoise are related to the processes that form it. Under these conditions, lead and strontium within turquoise may be derived from its immediate environment, and thus, any major impurities would be expected to have a
similar isotopic signature.

**Turquoise from the Redtail site: a case study**

The potential advantages of applying lead and strontium isotopes to questions of turquoise provenance can be demonstrated through a case study. The goal of the analyses described here is to identify the source of turquoise recovered from the Redtail site (AZ AA:12:149), a Hohokam village located in the northern Tucson Basin and occupied between ca. AD 700 and AD 950 (Fig. 1; Bernard-Shaw 1989; Klucas 2007). Over 3,000 fragments of turquoise have been recovered from the Redtail site and over 60 percent of this material has been classified as unworked turquoise, turquoise debitage or manufacturing debris. The quantity, form and distribution of turquoise across the site has been interpreted as evidence that the inhabitants of Redtail were involved in the acquisition and processing of turquoise during the Cañada del Oro Phase, in the early Hohokam Colonial period (AD 760–820) (Bernard-Shaw and Hohmann 1989). Thus, Redtail may have been part of an early exchange network involving turquoise in the region (Bernard-Shaw and Hohmann 1989).

The closest documented source of turquoise to the Redtail site can be found on the periphery of the Silver Bell Mountains, which lie about 56 km to the northwest of the site (Fig. 1). In addition to being the closest known source of turquoise to Redtail, the Silver Bell Mountains contain a prehispanic turquoise mining and habitation site that also dates to the Cañada del Oro Phase (Slawson 1997). This site, called Scorpion Village (AA:10:22), lies close to outcrops of turquoise, and thousands of fragments of the mineral were recovered from pit houses at the site, along with processing tools such as
drills, anvils and slab abraders (Slawson 1997). Notably, detailed documentation of these mines and their associated archaeological sites postdates many previous studies of turquoise exchange and provenance. The Silver Bell Mountains are not mentioned as a prominent source in any of the previous literature examining the turquoise trade (e.g. see Weigand and Harbottle 1993). This disparity highlights the problems that can arise from having an incomplete knowledge of prehispanic turquoise mining across the American Southwest and Mexico.

Because of the spatial proximity and temporal overlap of these two sites, Vokes and Gregory (2008) suggest that turquoise found at the Redtail site could have been mined in the Silver Bell Mountains. To test this idea, we apply lead and strontium isotopic measurements to turquoise samples recovered from the Redtail site and Scorpion Village. This comparison is based on the assumption that the collection of turquoise excavated from Scorpion Village derives from the prehispanic mines of the Silver Bell Mountains. If turquoise recovered at the Redtail site was mined from this area, the lead and strontium isotopic ratios of samples collected from both sites should be similar.

**Sample selection and methods**

To make the comparison, lead and strontium isotopic measurements were applied to 10 samples of turquoise from Scorpion Village and 17 samples of turquoise from the Redtail site. The lead and strontium isotopic analyses applied in this study are bulk analyses, which require the dissolution of a small amount of turquoise powder (typically between 25 and 100 mg). Bulk analyses have been critiqued because they limit the ability to control for impurities (Hull et al. 2008). Thus, to address this critique and better assess
the effect of impurities, the samples selected for study included raw and worked turquoise objects that varied visibly in quality, purity, and colour (Fig. 2). Minimal effort was made to remove impurities prior to analysis.

To confirm that these objects contain turquoise (and not another, similar-looking blue-green mineral), a subset of the samples was analysed with scanning electron microscopy using an energy-dispersive X-ray attachment (SEM-EDX). This technique produces semi-quantitative data on the concentrations of major elements. All samples tested contained copper, data collected via SEM-EDX also revealed the presence of other elements within the turquoise, especially silicon (Si) and calcium (Ca), further demonstrating the heterogeneous nature of the turquoise mineralisation.

All samples were powdered using a clean mortar and pestle and dissolved using twice-distilled ultra-pure hydrochloric acid (HCl). HCl was chosen because it dissolves turquoise, but will not digest many of the other mineral phases that may be present, especially silicates. Thus, the use of HCl to dissolve samples decreases the influence of non-turquoise minerals on the isotopic signature. However, to gather additional data to assess whether or not the impurities associated with the samples would alter the lead and strontium isotopic signature, we re-sampled five objects from Scorpion Village and dissolved the powders using a combination of hydrofluoric (HF), nitric (HNO3), and hydrochloric acids (see Table 2). While HCl should primarily dissolve the turquoise, the use of HF + HNO3 + HCl will fully digest all major mineral phases present. The details of the procedures used to prepare all the samples and to measure the isotopic ratios are reported in the technical appendix.
**Results and interpretations**

The lead and strontium isotopic ratios of all objects in this study are listed in Table 2 and presented in Figure 3. To visually display the results, the data are plotted according to the ratios $^{87}\text{Sr}/^{86}\text{Sr}$, $^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$, and $^{208}\text{Pb}/^{204}\text{Pb}$. As predicted, the measured lead and strontium isotopic ratios on samples from both Scorpion Village and the Redtail site are very similar to one another. Although not all combinations of measured isotope ratios are plotted due to space considerations, any chosen pair of ratios will produce similar results. Thus, turquoise found at the Redtail site has lead and strontium isotopic compositions that are consistent with an origin in the Silver Bell Mountains.

Additionally, these data can be interpreted to support the use of lead and strontium isotopes to fingerprint turquoise and to suggest that bulk analyses do not pose a significant problem when using these tracers. The samples reported here, especially from Scorpion Village, have a wide range of visual characteristics, including colour, hardness and the relative proportion of matrix minerals and host rock associated with the turquoise. Despite these differences among samples, the isotopic composition of the turquoise (or more accurately, turquoise-bearing) samples from both the Redtail site and Scorpion Village vary within roughly the same parameters. Even when five objects were re-sampled and completely dissolved for analysis, these values closely corresponded with the values measured from only dissolving the sample in HCl (for example, compare SB4a to SB4b in Table 2).

Although we only measure archaeological samples in this study, it is intriguing to
note that published lead isotopic measurements made on galena and molybdenite from the Silver Bell Mountains closely align with values we report for turquoise from Scorpion Village and the Redtail site (Bouse et al. 1999; Fig. 3a). This observation further supports the conclusion that turquoise at Scorpion Village and the Redtail site come from the Silver Bell Mountains, as it is expected that the turquoise would broadly reflect the isotopic characteristics of the metal-rich geologic environment in which it formed. The agreement between the archaeological evidence and the geochemical data supports the conclusion that turquoise at Redtail was likely to have been mined in the Silver Bell Mountains and demonstrates that lead and strontium isotopes can be effective tracers of turquoise. Although destructive, and therefore not appropriate for all archaeological objects, this method can be applied to a wide range of turquoise mineralisation, allowing for the analysis of weathered, poor quality or matrix-rich turquoise. The use of bulk analyses also confers the advantage of measuring isotopic ratios with high precision and accuracy via well-established and routine methods of analysis. This ability to collect high precision data is likely to be a significant advantage to differentiating between the numerous turquoise deposits across the American Southwest.

Conclusions and future directions

Measurements of turquoise collected from mines around the American Southwest have been shown to have distinct ranges of lead and strontium isotopic ratios, but a detailed discussion of these data is beyond the scope of this paper (Thibodeau et al. 2007a, 2008, 2011). However, to offer a necessary perspective on the data and conclusions drawn here, Figure 3b uses a multi-isotope plot to compare the lead and
strontium isotopic ratios of samples of the turquoise reported in this study to ranges of ratios collected on turquoise samples from five mines in the American Southwest. This figure demonstrates that the range of values measured on samples from the Redtail site and Scorpion Village is relatively small when compared to the array of ratios measured from other mines and locales.

The application of lead and strontium isotopes to turquoise offers a new opportunity to address longstanding questions about the origins of turquoise artefacts. High precision measurements of these two tracers have the potential to overcome the problems that have negatively impacted past studies of turquoise provenance, and may be robust enough to identify the source of samples with a wide range of compositional characteristics and associated impurities. Sourcing a complex mineral such as turquoise will continue to provide challenges for researchers for decades to come, and the continued destruction of the prehispanic mining record in the American Southwest makes studies of turquoise procurement particularly urgent. Although many turquoise mines have been abandoned or destroyed, the turquoise objects created by prehispanic cultures endure, capturing the imagination of the public and the scientific establishment alike. Through careful and systematic scientific analysis, it should be possible to begin to understand these objects, and the people who created them, from a new, isotopic perspective.

Technical appendix: methodology

To prepare samples for analysis, each was powdered using a clean mortar and pestle and accurately weighed. Because fragments of turquoise from Redtail were small
in size, in some cases, multiple pieces were combined to ensure enough material was present for isotopic analysis. Typical sample sizes ranged between 15 and 100 mg. All acid solutions used during sample preparation, separation and analysis were made from twice-distilled acid and ultra-pure Milli-Q water (Millipore, 18.2 MW). Powders were transferred to clean Teflon vials and dissolved on a hot plate at 125 °C using concentrated HCl, or in several steps using a combination of HF, HNO3 and HCl. After dissolution, lead and strontium are separated from single samples using Sr-Spec resin (Eichrom, Darien IL). Lead isotope analysis is conducted on a GV-Instruments MC-ICP mass spectrometer at the University of Arizona. Procedures for lead isotope analysis are detailed in Thibodeau et al. (2007c). The maximum 2s external errors associated with the measurements are 0.035% for $^{206}\text{Pb}/^{204}\text{Pb}$, 0.035% for $^{207}\text{Pb}/^{204}\text{Pb}$, 0.037% for $^{208}\text{Pb}/^{204}\text{Pb}$, 0.021% for $^{208}\text{Pb}/^{206}\text{Pb}$, and 0.009% for $^{207}\text{Pb}/^{206}\text{Pb}$.

After separation, strontium samples are loaded onto degassed tantalum (Ta) filaments using phosphoric acid and tantalum gel to enhance ionisation. All samples were analysed in a VG Sector 54 multi-collector thermal ionisation mass spectrometer in dynamic collection mode at the University of Arizona. The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios are corrected for mass fractionation of using $^{86}\text{Sr}/^{88}\text{Sr} = 0.1194$. The average $^{87}\text{Sr}/^{86}\text{Sr}$ value of the NBS-987 standard (all runs combined) is $0.71024 \pm 0.000016$ (n=14, 1s), based on 50–100 cycles of dynamic data collection. Total process blanks were prepared alongside all samples, and were an insignificant proportion of the total lead and strontium extracted from each sample.
Acknowledgements

All samples analysed in this study were curated at the Arizona State Museum in Tucson, Arizona. Mark Baker provided assistance in the laboratory. Lisa Molofsky and two anonymous reviewers read earlier versions of this paper, and greatly improved its final content.

References


Great Basin Anthropology 2: 245–256.


New Mexico and Ancient City Press, 93–128.


<table>
<thead>
<tr>
<th>Mineral</th>
<th>Formula</th>
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<tbody>
<tr>
<td>Turquoise</td>
<td>$\text{CuAl}_6(\text{PO}_4)_4(\text{OH})_8\cdot4\text{H}_2\text{O}$</td>
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<tr>
<td>Chalcosiderite</td>
<td>$\text{CuFe}_6(\text{PO}_4)_4(\text{OH})_8\cdot4\text{H}_2\text{O}$</td>
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<tr>
<td>Aheylite</td>
<td>$\text{FeAl}_6(\text{PO}_4)_4(\text{OH})_8\cdot4\text{H}_2\text{O}$</td>
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<tr>
<td>Fausite</td>
<td>$\text{ZnAl}_6(\text{PO}_4)_4(\text{OH})_8\cdot4\text{H}_2\text{O}$</td>
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<tr>
<td>Planerite</td>
<td>$\text{Al}_6(\text{PO}_4)_2(\text{PO}_3\text{OH})_2\cdot4\text{H}_2\text{O}$</td>
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<tr>
<td>unnamed</td>
<td>$\text{Fe}^{2+}\text{Fe}^{3+}_6(\text{PO}_4)_4(\text{OH})_8\cdot4\text{H}_2\text{O}$</td>
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</table>

(Source: Foord and Taggart, 1998)
Table 2. Lead and strontium isotopic ratios of turquoise samples from the Redtail site and Scorpion Village.

<table>
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<tr>
<th>Lab ID</th>
<th>FN#</th>
<th>Feature</th>
<th>dissolution method</th>
<th>87Sr/86Sr</th>
<th>% std err</th>
<th>(^{208})Pb/(^{204})Pb</th>
<th>(^{207})Pb/(^{204})Pb</th>
<th>(^{206})Pb/(^{204})Pb</th>
<th>(^{207})Pb/(^{204})Pb</th>
<th>(^{208})Pb/(^{204})Pb</th>
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<tr>
<td><strong>Scorpion Village (AZ:AA:10:22)</strong></td>
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<tr>
<td>SB1</td>
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<td>HCl</td>
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<td>0.8415</td>
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Figures

Figure 1. Locations of turquoise sources and archaeological sites from the American Southwest that are discussed in the text. Many additional sources (not shown here) can be found across central and northern Nevada (Morrissey 1968), and in Colorado (Modreski and Murphy 2002), as well as in Arizona, New Mexico and Sonora. All sources shown have evidence of prehispanic mining.
Figure 2. Examples of turquoise objects investigated for this study. At top is a turquoise artefact from Scorpion Village that shows variable colouration and the close association of turquoise with alunite; at bottom are turquoise fragments from the Redtail site showing the presence of considerable host rock attached to the turquoise.
Figure 3a.
Figure 3b.
Figure 3. Plots of lead and strontium isotopic ratios of turquoise objects from the Redtail site and Scorpion Village (data from Table 2). Data plotted for Scorpion Village include samples that underwent total and partial dissolution (see ‘Sample selection and methods’ section for discussion): shaded triangles represent samples that were dissolved in hydrochloric acid and open triangles represent those that were dissolved in a combination of hydrofluoric, nitric and hydrochloric acids. (a) Plot comparing the lead isotopic compositions \(^{206}\text{Pb}/^{204}\text{Pb} \text{ vs. }^{207}\text{Pb}/^{204}\text{Pb} \text{ and }^{206}\text{Pb}/^{204}\text{Pb} \text{ vs. }^{208}\text{Pb}/^{204}\text{Pb}\) of turquoise from the Redtail site to those of turquoise from Scorpion Village. Also shown are lead isotopic ratios reported for sulphide minerals (galena and molybdenite) from the Silver Bell Mining District (Bouse et al. 1999). Except where shown, symbols are larger than 2s external errors associated with the measurements. (b) Multi-isotope plot \(^{87}\text{Sr}/^{86}\text{Sr} \text{ vs. }^{208}\text{Pb}/^{204}\text{Pb}\) comparing isotopic ratios of turquoise from the Redtail site to isotopic ratios of turquoise from Scorpion Village. These measurements are contrasted with shaded regions that represent the isotopic signatures of turquoise from five other turquoise mining areas in the American Southwest. These geological data are part of a larger isotopic investigation of turquoise (being prepared by Thibodeau and colleagues) that is not part of this study. Locations of the turquoise sources are shown in Figure 1. All data points and shaded regions are larger than the 2s external errors associated with measurements.
APPENDIX C: ISOTOPIC EVIDENCE FOR THE PROVENANCE OF TURQUOISE IN THE SOUTHWESTERN UNITED STATES

To be submitted to the journal *GSA Bulletin*
ISOTOPIC EVIDENCE FOR THE PROVENANCE OF TURQUOISE IN THE SOUTHWESTERN UNITED STATES

Alyson M. Thibodeau¹, David J. Killick², John T. Chesley¹, and Joaquin Ruiz¹

¹Department of Geosciences, University of Arizona
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Abstract

Turquoise was widely traded among Prehispanic societies in the Southwest United States and Mexico, but the social and economic networks that mediated turquoise procurement and exchange remain largely unknown. Identifying the source of turquoise artifacts would provide insight into these networks and answer many longstanding questions about the source of turquoise found in archaeological sites that are distant from known mines. Here, we present new evidence that lead and strontium isotopic analysis can be used to identify or constrain the geologic provenance of turquoise. Lead and strontium isotopic ratios were measured on 116 samples of turquoise from 17 deposits across the Southwest United States and northern Mexico. These data reveal a wide range of isotopic variation among turquoise sources and define unique ‘fingerprints’ for many of the mining areas examined. Furthermore, these isotopic signatures are shown to vary geographically across the Southwest according to regional differences in the geologic settings of turquoise deposits. Lead and strontium isotopic analysis are thus powerful tools for determining the provenance of turquoise and provide a new way to investigate
archaeological questions about the procurement and exchange of the mineral in Prehispanic North America.

**Introduction**

Most North American turquoise deposits are in the southwestern United States (U.S.) and northern Mexico (Pogue, 1972; Sigleo, 1975). However, turquoise appears over a much wider area in the archaeological record and turquoise artifacts are often found hundreds (Pepper, 1909; Windes, 1992), and sometimes thousands (Saville, 1922) of miles from known mines. The sources of these artifacts remain an important question for archaeologists seeking to understand ancient economic and social networks. The ability to identify the source of turquoise found in the archaeological record would provide insight into these networks and offer answers to longstanding questions about turquoise procurement and exchange in Prehispanic North America.

Turquoise $[\text{CuAl}_6(\text{PO}_4)_4(\text{OH})_8\cdot4\text{H}_2\text{O}]$ is a blue-green copper-aluminum phosphate that primarily forms in the oxide zone of copper deposits in arid regions of the globe. In the Southwest U.S. and Mexico, Prehispanic artisans fashioned turquoise into beads and pendants, inlaid it into shell and bone ornaments, and tessellated tiles to form intricate mosaics. The significance of the mineral to Southwestern societies is underpinned by its presence in dedicatory caches for kivas and high status burials. At Pueblo Bonito, the largest Great House in Chaco Canyon, over 50,000 turquoise artifacts were recovered from a single mortuary crypt as part of the richest burial ever excavated in the Southwest (Plog and Heitman, 2010; Pepper, 1909). Turquoise was also highly prized in Mesoamerica, where has been reported in status burials from Guerrero, Jalisco, Morelos,
and Zacatecas (Weigand, 1992). During the Postclassic (~900-1521 CE), it became a preferred component of elaborate mosaic masks, shields, and other ceremonial and status objects, especially among Aztec royalty (Berdan, 1987; McEwan et al., 2006).

Turquoise was undoubtedly an important component of the ancient social and economic networks that operated among Southwestern societies and external demand for the mineral is believed to have stimulated their contact with Mesoamerican civilizations to the south (Weigand and Harbottle, 1993). Despite its undisputed significance in this regard, few specifics are known about the procurement and circulation of turquoise in prehistory. Archaeological evidence of Prehispanic turquoise mining extends from the Halloran Hills of southeastern California (Leonard and Drover, 1980; Blair and Winslow, 2004) to the Cerrillos Hills of northern New Mexico (Warren and Mathien, 1985; Warren and Weber, 1979; Mathien, 1998), and from central Nevada and southern Colorado (Modreski and Murphy, 2002; Morrissey, 1968) to the states of Sonora and Zacatecas in Mexico (Weigand, 1994; Fig. 1). However, detailed archaeological studies of these mines are rare (Warren and Mathien, 1985; Leonard and Drover, 1980) and little is known about the timing of their exploitation and the ultimate distribution of the extracted gems.

This study assesses the potential of lead (Pb) and strontium (Sr) isotopic analyses as tools to investigate the provenance of turquoise in archaeological sites across the Southwest U.S. and Mexico. Separately, these tracers have been applied, with different degrees of success, to determine the provenance of wide range of archaeological materials in the Southwest, including glaze-paints (Aggarwal et al., 2008; Huntley et al., 2007; Habicht-Mauche et al., 2000), architectural timbers (English et al., 2001; Reynolds
et al., 2005), human bone (Ezzo and Price, 2002), faunal remains (Grimstead, 2011), and ceramics (Carter et al., 2011). However, these tracers are rarely combined in archaeometric studies, and with the exception of one small exploratory study utilizing lead isotopes (Young et al., 1994), have never been applied to turquoise.

The first scientific campaigns to identify the source of turquoise from archaeological sites emerged in the 1970s and employed trace element analysis to infer links between artifacts and mines (Sigleo, 1975; Weigand et al., 1977). For over three decades, trace element analysis remained the dominant technique applied to questions of turquoise procurement (Mathien, 1981; Kim et al., 2003), but the data associated with the most extensive program of analyses were never published (Weigand, 1994; Weigand and Harbottle, 1993; Harbottle and Weigand, 1992; Weigand et al., 1977). It is thus not possible to independently evaluate the validity of many popular, but ultimately unsubstantiated ideas about ancient turquoise procurement and exchange. Moreover, subsequent studies were unable to identify characteristic trace elements profiles for turquoise sources (Mathien and Olinger, 1992). From a geological perspective this is hardly surprising, as turquoise is typically poorly crystallized, forms multiple solid-solution series, contains many impurities, and is closely associated with a variety of other minerals (Foord and Taggart, 1998; Thibodeau et al., in press).

Furthermore, trace element data may have limited utility because they provide little information about the geologic setting or origin of various turquoise deposits. This feature of trace element fingerprinting is disadvantageous because (1) turquoise mineralization is widespread across the Southwest and (2) there is incomplete
information about which deposits were exploited by ancient miners. Turquoise sources can vary significantly in their geographic extents: some sources contain only a few outcrops or mines (e.g. Welch and Triadan, 1991), while in others mineralization is spread over several to several tens of square miles (e.g. Leonard and Drover, 1980). Most importantly, many Prehispanic mines have been significantly altered, buried, and, in some cases, destroyed by later historical or modern mining activity. Because of this, it will never be possible to find and "fingerprint" every Prehispanic turquoise mine in the Southwest U.S. and Mexico. Recently, new efforts to chemically fingerprint turquoise sources have employed hydrogen and copper isotopic analyses (Hull et al., 2008). Although innovative, so far this approach also remains largely descriptive, offering no links between isotopic ratios of turquoise and the geographic distribution or geologic setting of specific mines.

In this paper, we show that high-precision measurements of lead and strontium isotopic ratios can be used to distinguish between turquoise deposits across the Southwest U.S. and Mexico. The strength of this approach lies in the fact that isotopic ratios of lead and strontium not only provide a fingerprint for sources, but also preserve information about the geological histories of both the rocks and ore deposits that are associated with turquoise mineralization. Across the Southwest U.S. and northern Mexico, turquoise deposits have formed by the weathering of different types of copper, phosphorous, and aluminum-bearing rocks that have different ages, geological histories, and isotopic compositions. As supergene processes do not measurably fractionate lead or strontium isotopes, any isotopic variations in these elements are inherited from the weathering of
the surrounding geologic environment. We are able to show that lead and strontium isotopic signatures of turquoise deposits pattern according to regional variations in the isotopic composition and geologic setting of nearby copper mineralization, associated igneous rocks, or their hosts. This link, between the isotopic composition of turquoise and its geologic setting, will be advantageous when interpreting the provenance of archaeological samples because it will permit inferences to be made about the source of an artifact even if its isotopic ratios cannot precisely be matched with that of a known mine.

We have already published a successful case study in which we are able to identify the source of turquoise found at an archaeological site near Tucson, Arizona (Thibodeau et al., in press). Here, we report the lead and strontium isotopic ratios measured on geologic samples of turquoise collected from mining districts across Arizona, New Mexico, Colorado, Nevada, and California in the U.S. and the state of Sonora in Mexico. We do not use the data presented here to address a specific archaeological question but instead to (1) demonstrate that lead and strontium isotopic ratios are robust discriminators of turquoise sources, and (2) lay a new foundation for the investigation of turquoise procurement and exchange by Prehispanic groups across North America.

**The Geologic Setting of Turquoise Mineralization in the Southwest U.S.**

The major turquoise deposits of North America are clustered in the southwestern United States, across Arizona, New Mexico, Colorado, Nevada, and southern California, and in Sonora, northern Mexico (Fig. 1). Turquoise is a secondary mineral formed from
the interaction of meteoric waters with copper, phosphorous, and aluminum-bearing rocks. It is rarely found below 30 meters of the surface and commonly occurs as veins, nodules, and open-space fillings in highly weathered and fractured felsic igneous rocks, especially monzonites, latites, and trachytes. Often igneous rocks that host turquoise are similar in age to the source of the copper, which may be in the form of chalcopyrite or cupriferous pyrite (Paige, 1912; Pearl, 1941). The oxidation of pyrite or other sulfides by meteoric waters and the subsequent generation of strong sulfuric acid is thought to be essential to leaching the phosphorous required for turquoise formation (Paige, 1912; Akright, 1979; Crook, 2002). In most of the deposits considered here, the source of phosphorous for turquoise is inferred to be accessory apatite, and possible sources of aluminum include potassium feldspar, kaolinite, or sericite.

In the Southwest U.S., turquoise is generally associated with geographically dispersed copper deposits and with silicic igneous rocks that have different ages and tectonic settings. In California, Arizona, western New Mexico, and northern Mexico, turquoise principally occurs within or around Laramide igneous complexes that are temporally and spatially associated with copper porphyry mineralization. In contrast, turquoise deposits in central New Mexico and southern Colorado are associated with igneous rocks and copper deposits of mid-Tertiary age. In these regions, turquoise has formed via the weathering of Oligocene igneous complexes that are found on the eastern margin of the Cordillera and contain alkalic rocks and Cu-Au-porphyry mineralization (McLemore, 1996; Kelley and Ludington, 2002). In southern Colorado, significant deposits of turquoise occur in early Oligocene volcanic rocks of the San Juan Volcanic
Field (Modreski and Murphy, 2002). In a subset of these sources, turquoise deposition has also occurred in Proterozoic rocks which are adjacent to or host copper deposits and their associated igneous rocks (Paige, 1912; Crawford and Johnson, 1937; Modreski and Murphy, 2002).

In a few cases, turquoise is found in more unusual contexts. For example, turquoise at the Sleeping Beauty and Castle Dome mines in Arizona’s Globe-Miami district is primarily found as veins in a highly fractured quartz monzonite of Proterozoic age, although the source of copper in this system is associated with a Late Cretaceous granite (Peterson, 1962; Peterson, 1954; Creasey, 1980). Turquoise from the Canyon Creek mines on the Fort Apache Reservation in Arizona occurs as nodules in the Dripping Springs Quartzite, a unit in the Apache-group sediments of Late Proterozoic age. The source of copper for turquoise at Canyon Creek is likely a copper-bearing Late Proterozoic diabase in the vicinity (Moore, 1968). In the Jarilla Mountains of southern New Mexico, which host the Orogrande mining district, turquoise is found in two geologically distinct contexts. In one locale, it occurs as veins within a highly weathered quartz-monzonite and in the other as nodules in Paleozoic shale (Lueth, 1998). In the latter location, the weathering of sedimentary phosphate minerals within the host shale contributed to the formation of the turquoise (Crook, 2002). We also note that turquoise mineralization is abundant in central and northern Nevada, where is it is found in sedimentary rocks (limestone, shale, chert), intrusive igneous rocks, and metamorphic rocks (Morrissey, 1968). Because of the large number of deposits and the paucity of information about the extent of Prehispanic mining activity in the Great Basin, we do not
systematically investigate turquoise from central or northern Nevada as part of this study. However, we do report isotopic ratios for turquoise collected from the Royston district which lies in west-central Nevada (Fig. 1) and comment on the potential for deposits in this region to have discriminating lead and strontium isotopic ratios.

These various geologic settings have allowed turquoise to form via the weathering of rocks that have a wide range of lead and strontium isotopic compositions. $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of igneous rocks reflect variations in their ages, sources, and chemical compositions. Strontium isotopic variation has been observed in silicic igneous rocks across a number of Laramide complexes (Farmer and DePaolo, 1984; Anthony and Titely, 1988; Lang and Titley, 1998), and in Oligocene igneous rocks from Colorado (Varga and Smith, 1984; Lipman et al., 1978) and northern and central New Mexico (Johnson and Lipman, 1990; Allen and Foord, 1991). Lead isotopic ratios of igneous rocks are also sensitive to age, source, and composition and, because lead and copper behave in a similar manner in hydrothermal fluids, are often used to infer the source of metals in ore deposits (Bouse et al., 1999).

One of the most important controls on the lead isotope geochemistry of Laramide copper porphyry deposits and their associated silicic igneous rocks is their location within different Proterozoic crustal provinces in the Southwest (Fig. 1). The Southwest U.S. is underlain by Proterozoic crust that formed between about 1.65 and 1.8 Ga (Wooden and DeWitt, 1991; Whitmeyer and Karlstrom, 2007; Wooden and Miller, 1990; Karlstrom et al., 2004), but isotopic measurements of outcropping Proterozoic rocks reveal that lead within discrete segments of this crust has evolved from different initial lead isotopic
compositions under different time-integrated $\mu$ ($^{238}\text{U}/^{204}\text{Pb}$) and $\kappa$ ($^{232}\text{Th}/^{238}\text{U}$) values (Wooden and DeWitt, 1991; Wooden and Miller, 1990). Lead isotopic ratios of sulfide minerals in Laramide porphyry copper deposits and their associated silicic igneous rocks reflect these variations, and are inferred to have inherited lead from basement rocks or their sources (Bouse et al., 1999). As turquoise is a common supergene mineral in Laramide copper porphyry deposits, we expect turquoise in these locations to broadly mirror these variations. Thus, crustal provinces within the Southwest, as defined by lead isotopes, provide a secondary framework to interpret the source of turquoise based on lead isotopic ratios.

Currently, there are fewer lead isotopic data available for mid-Tertiary ore deposits and volcanic rocks in New Mexico. Data on mineralized alkaline or silica-oversaturated igneous rocks of direct relevance to this study (such as those associated with copper and turquoise deposits in the Cerrillos or Orogrande districts) are mostly lacking. However, we are able to compare our lead isotopic data on Cerrillos turquoise to that of lead mineralization in the district (Thibodeau et al., submitted) and utilize lead and strontium isotopic measurements made on igneous rocks within the San Juan Volcanic Field to contextualize our isotopic data on turquoise from southern Colorado (Doe et al., 1979; Lipman et al., 1978; Varga and Smith, 1984).

It is worth acknowledging that turquoise deposits have traditionally been defined geographically in terms of “source areas” (Weigand and Harbottle, 1993; Sigleo, 1975; Welch and Triadan, 1991; Hull et al., 2008). This term emphasizes the importance of geography to archaeological questions of provenance but also captures the nature of
turquoise mineralization, which can be disseminated over tens of square miles. In most cases, these source areas, as historically defined, correlate with a set of turquoise mines and occurrences that broadly share a common geological setting. However, we caution that the correlation between the geography of these sources areas and the geologic setting of individual mines within them can sometimes be variable and complex.

**Samples and Methods**

We measured the lead and strontium isotopic ratios of 116 samples of turquoise from seventeen geographically widespread mining districts across southeastern California, southern Nevada, Arizona, New Mexico, and Colorado. Where appropriate, we identify turquoise source areas by using the name of the associated copper deposit or mining district (Fig. 1, Table 1). Data on turquoise from an 18th mining district (the Silver Bell district) is also discussed in this paper, but is taken from a previous study (Thibodeau et al., in press). Although turquoise has been recorded in a larger number of deposits in the Southwest (Anthony et al., 1995; Northrop, 1959; Morrissey, 1968) we primarily focus on mining districts for which there is documentary or archaeological evidence to indicate or suggest mining by Prehispanic groups (Table 1).

In addition to samples collected directly in the field, a significant proportion of samples come from a collection of turquoise curated at the Museum of Northern Arizona. This collection was amassed by archaeologist Phil C. Weigand in the 1970s and 1980s during his efforts to survey and record the location of Prehispanic turquoise mines in the Southwest U.S. and Mexico. In most cases, we were able to analyze samples from multiple localities within a source area. However, because most samples represent
surface collections and many are museum specimens, we do not break down most source areas into individual mines or localities (Table 1). As our primary objective is to distinguish broadly among source areas, this approach both fits our interpretive goals and the realities associated with acquiring samples. However, in a few cases, we identify specific mines or localities within source areas if these mines represent well-known locations with extensive ancient mining activity (e.g. Ithaca Peak in the Mineral Park district or Mt. Chalchihuitl in the Cerrillos district, see Table 1).

Past investigators have expressed concern that the analysis of bulk samples (that is, samples which require dissolution) is problematic for investigations of turquoise provenance because the common presence of impurities within the turquoise may induce too much scatter in the results (e.g. Hull et al., 2008). We have designed this study to address such critiques, by selecting turquoise samples from each source area with a wide range of physical characteristics, including quality (hardness), purity, and color. In most cases, we have only modified samples if turquoise nodules or veins were attached to a significant amount of host rock. In these situations, samples were coarsely crushed and fragments of turquoise were handpicked under a binocular microscope.

Samples were prepared and analyzed between 2007 and 2012 in the Department of Geosciences at the University of Arizona. Typical sample weights ranged from 25 to 100 mg, depending upon estimates of their lead and strontium contents and the size of available specimens. Before analysis, all samples were rinsed in either ultra-pure Milli-Q (MQ) water or a very dilute (~.01 M) acetic acid solution to remove any external or particulate contaminants on the surface of the sample (samples rinsed in acetic acid were
subsequently rinsed in MQ water, as well). After drying, all samples were ground in a clean alumina mortar and pestle, weighed, and dissolved with twice-distilled acid. Most samples were dissolved in capped Savillex vials with several milliliters of concentrated HCl, which effectively targets turquoise, but will not digest any silicate minerals present. All samples were left on a hotplate for at least 24 h at ~125°C. As a comparison, some samples (n=21) were completely digested using an HF step, an HNO₃ step, and an HCl step. By comparing the isotopic composition of samples from the same source areas that were dissolved with different reagents, we can better observe if impurities in bulk samples cause significant scatter in the isotopic signatures.

After dissolution, any undigested material was removed by centrifuging. Lead and strontium were separated from the same samples using Sr Spec resin (Eichrom). The procedures for lead isotopic analyses are detailed elsewhere (Thibodeau et al. 2007; 2012; in press). These samples were run over the course of five years and typical errors on $^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$, $^{208}\text{Pb}/^{204}\text{Pb}$ range from 0.02-0.04% at the 2σ level. These errors are calculated from the external reproducibility of the NBS-981 standard over the course of each measurement session. In the case of all samples reported here, external errors exceed the internal errors associated with the measurement of isotopic ratios in individual samples. Typical total process blanks for lead were between 100-250 picograms, an insignificant proportion of the total lead extracted from each sample.

Strontium isotopic ratios were measured on a VG Sector 54 multi-collector thermal ionization mass spectrometer in dynamic collection mode at the University of Arizona. The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios are corrected for mass fractionation using $^{86}\text{Sr}/^{88}\text{Sr}$
The percent standard error associated with individual $^{87}\text{Sr}/^{86}\text{Sr}$ measurements is reported in Table 2, because these errors occasionally exceed the external reproducibility of the NBS 987 standard. The average $^{87}\text{Sr}/^{86}\text{Sr}$ value of the NBS-987 standard (over all runs) is $0.710258 \pm 0.000012$ (n=27, 1σ), based on 50-100 cycles of data collection.

**Results and Discussion**

As described above, the data collected for this study (Table 2) represents measurements made on samples of turquoise with a wide range of qualities, purities and colors. We observe that turquoise samples dissolved using HF +HNO$_3$+ HCl have similar isotopic compositions to samples from the same source area dissolved with only HCl (see Table 2). Thus, the following description and discussion of isotopic variability among turquoise sources in the Southwest includes all data listed in Table 2.

In total, $^{87}\text{Sr}/^{86}\text{Sr}$ ratios measured on turquoise samples display a wide range of variation (0.706 to 0.831, Table 2). Lead isotopic ratios also widely vary with $^{206}\text{Pb}/^{204}\text{Pb}$ ratios between 17.24 and 23.57, $^{207}\text{Pb}/^{204}\text{Pb}$ ratios between 15.46 and 16.04, and $^{208}\text{Pb}/^{204}\text{Pb}$ ratios between 37.24 and 45.23 (Table 2). For the purpose of clearly presenting the discriminating potential and archaeological utility of this multivariate lead and strontium isotopic dataset, the turquoise source areas addressed in this paper are divided into three main groups for discussion, as shown in Figure 1 and Table 1. Group 1 includes Mineral Park, Halloran Springs, and Crescent Peak; Group 2 includes Silver Bell, Cananea, Gleeson, Courtland, Castle Dome, Morenci, Tyrone, and Sleeping Beauty; Group 3 includes Cerrillos, Orogrande, Eureka, the King Mine, and the Hall Mine. Due
to the distinctive geologic settings of turquoise deposits at Canyon Creek and the Royston
district, we discuss their isotopic ratios separately.

**Group 1: Turquoise Deposits of the Mojave Province**

Turquoise mineralization is abundant in a number of mining districts that fall at
the juncture of the Arizona, California, and Nevada state-lines (Group 1; Fig. 1, Table 1).
Here, substantial archaeological evidence of Prehispanic mining has been recognized in
the Halloran Springs district of California (Leonard and Drover, 1980; Blair and
Winslow, 2004), on the south and west flanks of Crescent Peak in Clark County, Nevada
(Morrissey, 1968), and in the Mineral Park District on the western slopes of Arizona’s
Cerbat Mountains (Johnston, 1964; Sterrett, 1908). Although little is known about the
Prehispanic miners who worked these deposits, turquoise is extremely rare in
archaeological sites along the California coast and throughout the Nevada’s Great Basin.
Thus, the probable destinations for this turquoise lie in the Southwest or Mesoamerica
(Blair and Winslow, 2004).

The range of $^{87}\text{Sr}/^{86}\text{Sr}$ ratios measured on turquoise from each of these three
source areas greatly overlap with one another, varying between 0.7109 and 0.7213 (Fig.
2). This range of $^{87}\text{Sr}/^{86}\text{Sr}$ ratios also overlaps with source areas in southeastern Arizona,
western New Mexico, and northern Mexico (Fig. 2). However, we show below that
turquoise samples from Mineral Park, Halloran Springs, and Crescent Peak have lead
isotopic ratios that largely distinguish them from mines elsewhere in the Southwest. Their
distinctive lead isotopic composition reflects the occurrence of turquoise within


Proterozoic rocks of the Mojave Province and within Mesozoic igneous rocks that have inherited the isotopic characteristics of this terrane.

To demonstrate that the lead isotopic composition of turquoise mineralization broadly mirrors that of its geologic setting, we first consider the isotopic composition of turquoise from mines located in the Mineral Park district. Here, turquoise is primarily found in the weathered portions of Laramide quartz monzonite stocks that are associated with copper porphyry mineralization and have intruded into Proterozoic crystalline rocks of the Mojave Province. We were able to analyze samples from three localities within the Mineral Park district, including Ithaca Peak and Turquoise Mountain, which are both sites of extensive ancient mining activity (Johnston, 1964; Sterrett, 1908).

We observe that turquoise from each locality carries a distinct lead isotopic signature (Fig. 3, Table 1). The significant isotopic variation among localities within the Mineral Park district may seem, at first, to preclude the use of lead isotopic ratios to ‘fingerprint’ turquoise source areas. However, when considered in the context of existing lead isotopic data on sulfide minerals, Late Cretaceous stocks, and Proterozoic rocks from the Cerbat Mountains (Wooden and DeWitt, 1991; Bouse et al., 1999), it is apparent that turquoise from different areas of the Mineral Park district accurately reflects the distinctive isotopic characteristics of its geologic environment. Of these localities, turquoise from Ithaca Peak clearly has the least variable isotopic signature, with an average isotopic composition of $^{206}\text{Pb}/^{204}\text{Pb} = 17.99$, $^{207}\text{Pb}/^{204}\text{Pb} = 15.58$, and $^{208}\text{Pb}/^{204}\text{Pb} = 38.87$. These ratios are consistent with the known isotopic composition of chalcopyrite, pyrite, and galena from the Mineral Park porphyry copper deposit (Fig. 4; Bouse et al.,
and we can therefore infer that turquoise mineralization on Ithaca Peak may have incorporated lead from oxidized sulfide minerals.

Turquoise Mountain, historically referred to as Aztec Peak (Johnston, 1964; Sterrett, 1908), is located only ~1 mile south of Ithaca Peak, but contains turquoise with a distinct lead isotopic composition (Fig. 3). Most strikingly, the $^{208}\text{Pb}/^{204}\text{Pb}$ ratios of these turquoise samples are extremely high, ranging from ~43 to over 45. This unusual signature is explainable if Proterozoic rocks in the Mineral Park District are a source of lead in the turquoise which formed at Turquoise Mountain. Whole rock analyses of Proterozoic units from the Cerbat Mountains reveal at least one sample with a similar enrichment in $^{208}\text{Pb}$ (Wooden and Dewitt, 1991; Fig 3) making such an explanation plausible. A third locale for turquoise examined from the Mineral Park district, has lead isotopic ratios that are different from those of turquoise at Ithaca Peak and Turquoise Mountain, but fall well within the range of lead isotopic signatures reported for sulfides, stocks, and Proterozoic rocks in the Cerbats (Fig. 3). When all turquoise samples from Mineral Park are plotted on a $^{206}\text{Pb}/^{204}\text{Pb}$ vs. $^{207}\text{Pb}/^{204}\text{Pb}$ graph, they fall about the 1.7 Ga isochron defined for the Mojave Province by Wooden and DeWitt (1991) and Wooden and Miller (1990; Fig. 3). Thus, the widely variable signature of turquoise from specific mines in the Mineral Park district can be fully accounted for by considering the isotopic composition of rock units and sulfide mineralization in the immediate geological environment.

Turquoise samples from the Halloran Springs and Crescent Peak districts have similar lead isotopic ratios to turquoise from the Mineral Park district, which reflect their
weathering from a geologic environment with similar lead isotopic characteristics (Fig. 4). On a $^{206}\text{Pb}/^{204}\text{Pb}$ vs. $^{207}\text{Pb}/^{204}\text{Pb}$ graph, turquoise samples from Halloran Springs and Crescent Peak also scatter about the 1.7 Ga Mojave isochron (Fig. 4). Thus, the lead isotopic composition of turquoise from all three of these source areas accurately reflects their association with and derivation from rocks that have isotopic characteristics of the Mojave Province. Furthermore, while turquoise from Halloran Springs, Crescent Peak, and Mineral Park have some overlap in their isotopic fingerprints, each district has distinctive ranges of isotopic ratios which may make it possible, in some cases, to distinguish among turquoise from each of these source areas in the archaeological record (Fig. 4).

**Group 2: Turquoise Deposits of the Southeastern Arizona Province**

Several hundred miles away from the turquoise deposits of the Mojave Province, another major cluster of turquoise sources lies in southeastern Arizona and adjacent areas of parts New Mexico and Mexico (Group 2; Fig. 1; Table 1). Here, turquoise mineralization is found in the Tyrone, Morenci, Silver Bell, Courtland, Gleeson, and Cananea mining districts and the Sleeping Beauty and Castle Dome mines (both within the Globe-Miami district). Of these deposits, evidence of Prehispanic turquoise extraction has been identified at Sleeping Beauty, Tyrone, Silver Bell, Courtland, Gleeson, and Cananea (Table 1).

Except for turquoise from the Sleeping Beauty mine (discussed below), this group of deposits is characterized by a large range $^{87}\text{Sr}/^{86}\text{Sr}$ ratios that mostly overlap with those of turquoise from deposits in the Mojave Province (0.709-0.723; Fig. 2). However, lead
isotopic compositions of turquoise from these two groups of deposits are different (Fig. 5). Southeastern Arizona and its adjacent areas are underlain by basement rocks of the Southeastern Arizona Province (as defined by Bouse et al., 1999 and henceforth referred to as SEAZ, see Fig. 1). Here, lead isotopic ratios of Laramide porphyry copper deposits and their associated silicic igneous rocks are mostly different from those of the Mojave Province (Bouse et al., 1999). This contrast is preserved in the isotopic signatures of turquoise as shown in Figure 5. The best separation between turquoise from the Mojave Province (Group 1) and turquoise from the SEAZ Province (Group 2) can be seen on a $^{206}\text{Pb}/^{204}\text{Pb} \text{ vs.} ^{208}\text{Pb}/^{204}\text{Pb}$ graph (Fig. 5).

Bouse et al. (1999) use the lead isotopic compositions of Laramide ore deposits in the SEAZ Province to sub-divide it into north and south sub-provinces (Fig. 1). Igneous rocks and sulfide minerals in the northern sub-province generally have lower $^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$, and $^{208}\text{Pb}/^{204}\text{Pb}$ ratios than the southern sub-province (Fig. 6). The Morenci, Tyrone, Castle Dome, and Sleeping Beauty sources are found in the northern sub-province, while the Silver Bell, Courtland, Gleeson, and Cananea districts lie in the southern sub-province (Fig. 1). Notably, the lead isotopic ratios of turquoise from Tyrone, Morenci, and Castle Dome lie well within the range of sulfide minerals from the northern sub-province. The paucity of turquoise samples available from these source areas does not allow us to confidently define the range of lead isotopic ratios in each. However, the consistency of these values with the regional isotopic signature of sulfide mineralization indicates that turquoise samples from these source areas reflect their larger geologic and isotopic context. Notably, one sample from Tyrone (T3) clearly has more
radiogenic lead isotopic ratios than other samples from the same district. This sample was obtained from a museum collection, and is attributed only to the “Burro Mountains.” As the Tyrone district is just one of many locations within the Burro Mountains where turquoise is found (Gillerman, 1964), it is possible this sample derives from another, isotopically distinct, mining district in the range that contains turquoise. However, despite its offset from turquoise from the Tyrone district, the isotopic composition of T3 is still consistent with a source in the SEAZ Province.

In the south sub-province, we have sampled turquoise mineralization in the Silver Bell, Courtland, Gleeson, and Cananea districts. Turquoise samples from these areas tend to have elevated $^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$, and $^{208}\text{Pb}/^{204}\text{Pb}$ ratios compared to deposits to the north, consistent with the isotopic composition of sulfides associated with copper porphyry mineralization in most southeastern parts of Arizona (Fig. 6; Bouse et al. 1999). However, turquoise samples from the Courtland and Gleeson mining districts (both in the Dragoon Mountains) have an array lead isotopic ratios that are transitional between the signatures of the two sub-provinces. Turquoise from Gleeson appears to have a relatively constant isotopic signature with $^{206}\text{Pb}/^{204}\text{Pb}$ ratios between 17.81 and 18.07, $^{207}\text{Pb}/^{204}\text{Pb}$ ratios between 15.51 and 15.55, and $^{208}\text{Pb}/^{204}\text{Pb}$ ratios between 37.94 and 38.11. The least radiogenic samples analyzed from the Courtland district are isotopically similar to turquoise from Gleeson. However, some examples of Courtland turquoise have extremely elevated $^{206}\text{Pb}/^{204}\text{Pb}$ ratios (18.91-22.57; see Fig. 6). Because turquoise mineralization from the Courtland district occurs both in Cretaceous granite and Cambrian Quartzite (Crawford and Johnson, 1937) and other Proterozoic and Cambrian units outcrop in the
immediate vicinity, the variable geology is likely responsible for the wide ranges of ratios observed. It is notable that while $^{206}\text{Pb}/^{204}\text{Pb}$ ratios are elevated, the $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb}$ ratios in these samples remain relatively constant in comparison. This pulls the isotopic signature of many Courtland samples far to the right of trend formed by the sulfide and other turquoise data in Figure 6.

Sleeping Beauty turquoise has an unusual geologic context as it occurs in the Lost Gulch Quartz Monzonite, an igneous unit of Proterozoic age. However, the source of metals in the porphyry system at this mine is the Late Cretaceous Schultze Granite (Creasey, 1980; Peterson, 1962). Sleeping Beauty turquoise has extremely variable and radiogenic lead and strontium isotopic ratios that give it a unique signature (Table 1, Fig. 6). Lead isotopic ratios of turquoise samples from Sleeping Beauty are higher than observed in other deposits of the SEAZ Province, and while they have similar $^{206}\text{Pb}/^{204}\text{Pb}$ ratios when compared to samples from Courtland, their $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb}$ ratios are higher (Fig. 6). Sleeping Beauty turquoise also has extremely radiogenic $^{87}\text{Sr}/^{86}\text{Sr}$ ratios (0.753-0.831). Although we cannot directly identify the source of the strontium through the analysis of turquoise alone, the highly radiogenic strontium isotopic composition clearly indicates the source must be one or more of the Proterozoic rocks in the vicinity. This unique strontium isotopic fingerprint (among source areas in this study) should make it possible to easily identify Sleeping Beauty turquoise within the archaeological record.

*Group 3: Turquoise form Central Colorado and New Mexico*
Turquoise samples from deposits in central New Mexico and Colorado tend to have $^{87}\text{Sr}^{86}\text{Sr}$ ratios less than 0.710 (0.706-0.709) and thus their isotopic signatures can contrasted with those of turquoise from all source areas discussed above. With the exception of the Eureka district where turquoise occurs in a probable Laramide quartz monzonite, turquoise mineralization in these locations has formed via the weathering of igneous rocks of Oligocene age that were emplaced or erupted during the transition from compressional to extensional tectonics across the region (Kelley and Ludington, 2002). Although strontium isotopic signatures of these source areas overlap with one another and are thus not unique, lead isotopic ratios can clearly discriminate among turquoise from each of these deposits (Fig. 7). The combined use of lead and strontium isotopes thus provides each of these source areas with a unique signature. Compared to turquoise from source areas in both Groups 1 and 2, samples of turquoise from these deposits are observed to have less variable lead and strontium isotopic compositions, which may in part be explained by the lack of Proterozoic rocks that are associated with turquoise mineralization in these areas. In total, $^{206}\text{Pb}/^{204}\text{Pb}$ ratios range between 17.66-19.38, $^{207}\text{Pb}/^{204}\text{Pb}$ ratios range between 15.49-15.63, and $^{208}\text{Pb}/^{204}\text{Pb}$ ratios range between 37.42-38.99.

Among this group of turquoise source areas are the Cerrillos Hills, which contain a cluster of heavily worked Prehispanic turquoise mines including the Great Pit at Mt. Chalchihuitl, widely considered to be that largest ancient turquoise mine in the Southwest. First noted by Blake (1858), the mines of the Cerrillos district were likely the most significant source of turquoise in Prehispanic North America, and their archaeology
and geology has been widely examined and described (Carter et al., 2011; Warren and Mathien, 1985; Mathien, 1998; Schroeder, 1979; Milford, 1995; Warren and Weber, 1979; Blake, 1858). The Cerrillos Hills are primarily the eroded remnants of Oligocene monzonite stocks and volcanics of the Espinaso formation. The district contains ores of copper, lead, zinc that are directly related to the igneous activity (Disbrow and Stoll, 1957; Akright, 1979; Maynard, 2005), and turquoise deposits occur in areas of strong argillic alteration where the rock once contained high concentrations of primary pyrite (Akright, 1979). Turquoise deposits and extensive ancient mines are also found about six miles to the northeast of the main group of mines on a small knob known as Turquoise Hill (Milford, 1995).

Because of its importance, we have analyzed turquoise from several localities in the Cerrillos district, including Mt. Chalchihuitl and Turquoise Hill. Our analyses have revealed that turquoise mined from Mt. Chalchihuitl (and elsewhere in the Cerrillos district) is isotopically distinct from turquoise mined on Turquoise Hill. Samples from Mt. Chalchihuitl have an average $^{207}\text{Pb}/^{204}\text{Pb} = 15.584$ (± 0.015, 2sd), and $^{208}\text{Pb}/^{204}\text{Pb}$ values consistently below 38.50, while turquoise from mines on Turquoise Hill have an average $^{207}\text{Pb}/^{204}\text{Pb} = 15.622$ (± 0.009, 2sd) and $^{208}\text{Pb}/^{204}\text{Pb}$ values consistently above 38.5 (Table 1, Fig. 7). $^{206}\text{Pb}/^{204}\text{Pb}$ ratios are less diagnostic, but generally range to lower values in turquoise from the Cerrillos Hills than at Turquoise Hill (Table 1). Because turquoise from these two areas have distinct lead isotopic signatures (Fig. 7), it should be possible to resolve them as separate “sources” when interpreting the isotopic composition of turquoise from the archaeological record. Notably, the lead isotopic composition
Cerrillos turquoise is more variable than, but similar to that of galena from throughout the district (Thibodeau et al., submitted).

The isotopic fingerprint of turquoise from the Cerrillos source area is most similar to that of turquoise from the Orogrande district, where Prehispanic mines have also been recognized and turquoise is found as veins in quartz monzonite and as nodules in a shale unit of the upper Pennsylvanian to lower Permian Laborcita formation (Hidden, 1893; Lueth, 1998; Crook, 2002; North, 1982). However, at Orogrande, turquoise tends to have elevated $^{208}\text{Pb}/^{204}\text{Pb}$ relative to turquoise from Cerrillos (Fig. 7). The Little Hatchet Mountains, which host turquoise deposits of the Eureka district, also have extensive evidence of Prehispanic working. Here, turquoise is strongly associated with both jarosite and clay minerals, and found within highly-altered sodic facies of a monzonite of probable Laramide age (Lasky, 1947). Of the samples measured, the isotopic signature of turquoise from the Eureka district has lower $^{208}\text{Pb}/^{204}\text{Pb}$ values than turquoise from either the Cerrillos or Orogrande districts (Fig. 7).

Turquoise is also found in southern Colorado, at the King Mine in the near the town of Manassa and at the Hall mine near the town of Villagrove (Burroughs, 1972; Pearl, 1941; Modreski and Murphy, 2002). The King Mine lies a few miles west of the Rio Grande in the San Luis Valley and turquoise there is found in highly-altered silicic volcanic rocks which are likely equivalent to the Conejos formation of the San Juan Volcanic field (Modreski and Murphy, 2002). Evidence of Prehispanic mining has been discovered in this locale (Modreski and Murphy, 2002; Burroughs, 1972). Turquoise from the Hall Mine is described as occurring in silicic volcanic rock about five miles east
of the Bonanza Caldera, on the edge of the San Juan Volcanic Field (Modreski and Murphy, 2002). It is not known if there was any Prehispanic turquoise mining in this area.

Turquoise from both the King and Hall mines have lead isotopic ratios that are far less radiogenic than turquoise from either the Cerrillos or Orogrande districts, and the lead isotopic analyses presented here define unique signatures for both the King and Hall mines among all the turquoise deposits considered in this paper. The similar lead and strontium isotopic data from both these sources is broadly consistent with existing isotopic data for volcanic rocks of the San Juan Volcanic field (Lipman et al., 1978). Thus, although it is not known if turquoise from the Hall Mine was exploited in prehistory, the distinctive isotopic signature should make it possible to recognize this turquoise if it is present among archaeological samples.

*Turquoise from Canyon Creek, Arizona*

Among the deposits in this paper, the turquoise mines at Canyon Creek have a unique geologic context. Here, turquoise is found primarily as tiny nodules in the Dripping Springs Quartzite, which is a feldspar-rich, clastic member of the Proterozoic Apache Group (Granger and Raup, 1964). The Canyon Creek source comprises three discrete localities that lie within a few hundred meters of one another on the White Mountain Fort Apache Reservation, and all have archaeological evidence of Prehispanic mining activity (Welch and Triadan, 1991). At least two of these localities are associated with radioactive anomalies identified during areal surveys (Moore, 1968).

The $^{87}$Sr/$^{86}$Sr signature of the Canyon Creek samples examined for this study range
between 0.714 and 0.721. All but one of turquoise samples analyzed for this study come from the tailings of the northernmost quarry, and have extremely radiogenic lead isotopic ratios. Turquoise samples from this specific mine have $^{206}\text{Pb}/^{204}\text{Pb}$ ratios that range from 20.8 to greater than 23 and $^{207}\text{Pb}/^{204}\text{Pb}$ ratios that range to $\sim$15.75 to more than 16. The extremely high $^{207}\text{Pb}/^{204}\text{Pb}$ ratios (>15.9) observed in many of these samples have not been observed in turquoise from other source areas. $^{208}\text{Pb}/^{204}\text{Pb}$ ratios range from 40.07 to more than 42. The extremely radiogenic lead isotopic composition likely reflects the association of turquoise with the Dripping Springs Quartzite, which is known to contain many uranium deposits of Proterozoic age (Nutt, 1984). Notably, Welch and Triadan (1991) have identified the copper-uranium-phosphate metatorbernite in the turquoise deposits of the north quarry and suggest that the association between turquoise and metatorbernite may also be an identifying feature of this source.

Only one fragment of turquoise suitable for isotopic analysis was collected from the tailings of the other two mines at Canyon Creek. This piece of turquoise (CC-9) has a much less radiogenic lead isotopic signature: $^{206}\text{Pb}/^{204}\text{Pb} = 19.264$, $^{207}\text{Pb}/^{204}\text{Pb} = 15.657$, $^{208}\text{Pb}/^{204}\text{Pb} = 38.917$. The enormous difference between the isotopic signatures of these two mines indicates that further investigation will be needed to fully characterize turquoise from the Canyon Creek source. However, it is noteworthy that the isotopic ratios of all samples from this locale are constrained along a linear array on a $^{206}\text{Pb}/^{204}\text{Pb}$ vs. $^{207}\text{Pb}/^{204}\text{Pb}$ plot. A line regressed through all these points has a model age of about 1.3 Ga, which is roughly consistent with the late Proterozoic ages assigned to the Dripping Springs Quartzite and the diabase dikes that may have served as the source of
copper. Despite the contrasting signatures of turquoise from the two mines, the radiogenic lead isotopic ratios of turquoise from the northern quarry are extremely distinctive, and turquoise from this locale should be readily identified with isotopic analysis if present among archaeological samples.

**Turquoise from the Royston District, Nevada**

We only investigate the isotopic composition of one mining district from central Nevada, the Royston district (Fig. 1). Located in on the border of Esmeralda and Nye counties, it is among the most productive mining districts for turquoise in the state, and still produces today. Turquoise from the Royston district is characterized by relatively unradiogenic $^{87}$Sr/$^{86}$Sr ratios (0.70779-0.70810), but relatively radiogenic lead isotopic ratios ($^{206}$Pb/$^{204}$Pb > 19, $^{207}$Pb/$^{204}$Pb > 15.7, $^{208}$Pb/$^{204}$Pb > 39). Turquoise mineralization is found in a quartz monzonite porphyry of probable Late Triassic to Early Jurassic age (Seedorff, 1991). This unit is similar to a quartz monzonite porphyry in the nearby Crow Springs district, where prospects for turquoise are also known. The relatively radiogenic lead isotopic ratios of turquoise from Royston are similar to the isotopic compositions of Jurassic intrusions in the Great Basin described by Vikre (2000), and among the turquoise deposits considered in the paper, Royston has a unique isotopic signature (Fig. 7).

**Implications for Provenance Studies**

These results make clear that a multi-isotope approach is crucial to the determination of turquoise provenance as isotopic ratios of lead and strontium each separate different turquoise source areas and offer different degrees of resolution. Geographically clustered turquoise deposits across the Southwest U.S. and northern
Mexico share similar isotopic characteristics (e.g. Groups 1, 2, & 3, see Fig. 8). Isotopic differences between these clusters can be mostly ascribed to large-scale, regional variations in the tectonic and geologic setting of turquoise sources. Because turquoise was exchanged over long-distances in prehistory, lead and strontium isotopes are ideal for addressing questions of turquoise provenance at the scale required to answer many important archaeological questions. The geographic clustering of turquoise sources with similar isotopic characteristics should thus minimize ambiguity in archaeological interpretations about turquoise procurement and exchange.

Although the strontium isotopic signatures of most turquoise deposits are not unique, specific ranges of $^{87}\text{Sr}/^{86}\text{Sr}$ ratios (we suggest > 0.710 and < 0.710) appear to be characteristic of turquoise from different regions of the Southwest U.S. (Figs. 1 & 2). Turquoise from deposits associated with mid-Tertiary rocks in central New Mexico and Colorado have $^{87}\text{Sr}/^{86}\text{Sr}$ ratios less than 0.710, as does turquoise from the Eureka district in southwestern New Mexico (Group 3). The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of turquoise from the Royston district also overlaps with these values in strontium isotope space, suggestive of the possibility that other turquoise from north and central Nevada might have similar $^{87}\text{Sr}/^{86}\text{Sr}$ ratios as well. More radiogenic strontium isotopic compositions ($^{87}\text{Sr}/^{86}\text{Sr}$ > 0.710) are typical of turquoise associated with Laramide igneous and Proterozoic rocks across southeastern California, southern Nevada, Arizona, and western New Mexico (Groups 1 & 2; Figs. 1 & 2). The turquoise mines at Canyon Creek also have $^{87}\text{Sr}/^{86}\text{Sr}$ ratios greater than 0.710, and clearly group with these deposits in strontium isotope
space. Only Sleeping Beauty has a unique strontium isotopic fingerprint ($^{87}\text{Sr}/^{86}\text{Sr} = 0.7532-0.8309$).

Although it may be possible to further resolve deposits based on strontium isotopes, given the wide range of $^{87}\text{Sr}/^{86}\text{Sr}$ ratios that characterize many source areas, we feel more data is needed in order to confidently define complete strontium isotopic fingerprints. Whether the large amount of strontium isotopic variation in single source areas is a property of the turquoise itself, the result of impurities, or some combination of the two, we are unable to determine at this time. However, these broad differences in $^{87}\text{Sr}/^{86}\text{Sr}$ ratios are clearly reproducible features of these source areas, and offer important and reliable information about sample provenance.

Lead isotopic ratios separate out deposits differently than strontium, and when used in combination, provide the resolution necessary to uniquely fingerprint many sources areas, and sometimes, specific mines within them. For example, $^{87}\text{Sr}/^{86}\text{Sr}$ ratios cannot resolve the differences among most of the turquoise source areas in Arizona, California, southern Nevada, western New Mexico or Sonora (Groups 1 and 2 + Canyon Creek), but lead isotopic ratios both distinguish among these deposits at a regional scale (Figs. 5 and 8) and in many cases define characteristic signatures for individual source areas within them (Figs. 3 & 6). The better resolution offered by lead isotopes is even more apparent with respect to source areas that have $^{87}\text{Sr}/^{86}\text{Sr}$ ratios less than 0.710 (Cerrillos, Orogrande, Eureka, King Mine, Hall Mine, Royston). So far, lead isotopic ratios separate turquoise from all six of these source areas with no overlap (Fig. 7). Thus, when both lead and strontium isotopic ratios are taken into account, each of the six
sources has a unique isotopic fingerprint. In a few cases, lead isotopic ratios alone provide distinctive fingerprints source areas, and prominent sites of ancient mining within them. In particular, we note unique lead isotopic signatures for turquoise at Ithaca Peak and Turquoise Mountain in the Mineral Park district, many of the samples from Canyon Creek, and the King Mine in Colorado (Fig. 8).

The success of lead and strontium isotopes in resolving distinct fingerprints for many turquoise sources and mines clearly indicates that any impurities present do not cause enough scatter in lead and strontium isotopic ratios to preclude their use as tracers of turquoise. This conclusion is further strengthened by a previous case study in which lead and strontium isotopic ratios were successfully used to identify the source of turquoise artifacts found in an early Hohokam workshop in Arizona (Thibodeau et al., in press). In this previous study, we linked turquoise from this workshop to turquoise excavated from pithouses near Prehispanic mines on the periphery of the Silver Bell Mountains. This result confirms prior speculation by archaeologists that turquoise at this site (the Redtail site) was mined in the Silver Bell Mountains (Vokes and Gregory, 2008). The consistency of these isotopic data with archaeological expectations gives us further confidence that this methodology is robust and applicable to turquoise artifacts throughout the archaeological record.

Conclusions and Suggestions for Future Study

Lead and strontium isotopes are powerful tools with which to interpret Prehispanic turquoise procurement and exchange in the Southwest U.S. and Mexico. Based on these results, we conclude that (1) lead and strontium isotopic ratios are
effective discriminators of turquoise sources at multiple scales and (2) isotopic fingerprints of turquoise sources vary geographically based on broad-scale differences in their geologic settings. An isotope-based study thus permits an approach to archaeological questions of turquoise provenance that is geologically informed and can be directly quantified. Such an approach is ideal because turquoise deposits are numerous and the direct characterization of every outcrop or mine is not feasible. Furthermore, with this approach, it will be possible to make inferences about the sources of turquoise artifacts even if their lead and strontium isotopic signatures do not match precisely those that of any known mines.

This study represents the most comprehensive geochemical dataset published to date on geological samples of turquoise. However, we emphasize that the fingerprints presented here are not complete, and future research will be needed to either confirm or expand upon the range of isotopic ratios associated with each source area. Additional measurements will be especially important to characterize sources for which we only have one sample, or in which we have observed widely variable isotopic ratios (e.g. Tyrone/Burro Mountains and Canyon Creek). It will also be necessary to collect isotopic data on sources that were not included in this study, both elsewhere in the Southwest, across northern and central Nevada, and in Mexico. This larger dataset will allow researchers to better define archaeological questions that can be best addressed with this methodology. It will also help to determine if there are distant sources that share similar isotopic signatures, as such knowledge will be important when interpreting the source of artifacts. The widespread availability of high-precision lead and strontium isotopic
measurements should make it possible for multiple research groups to build this more complete framework together. Lead and strontium isotopes thus offer the possibility of re-addressing many long-standing questions about turquoise procurement and exchange in the Southwest U.S. and Mexico. Archaeological applications of this methodology are currently underway (e.g. Thibodeau et al., 2011; Thibodeau et al., in press) and have great potential to provide new insights into the connections among communities, cultures, and civilizations in Prehispanic North America.

Acknowledgements

This project was possible due to the cooperation, collaboration, and generosity of many people and organizations. The majority of the samples analyzed in this study come from a collection amassed by Phil C. Wiegand and curated at the Museum of Northern Arizona. Additional samples were provided the New Mexico Bureau of Mines and Mineral Resources. Samples from Villa Grove were provided by Peter Modreski. Dan Couvoisier of the Sleeping Beauty Turquoise in Globe, Arizona provided turquoise from the Sleeping Beauty mine and allowed us access to it. We are grateful to Bill Baxter, Todd Brown, and Doug Magnus for providing access to the turquoise mines of the Cerrillos District, and for sharing their vast knowledge of area with us. Thank you to Ed Nazelrod and Bob Reynolds for being guides to the turquoise mines of the Halloran Springs district, and for much help collecting turquoise there. We’d also like to thank John Welch and the White Mountain Apache tribe, especially Hon. Ronnie Lupe, Chairman, Mr. Ramon Riley, Cultural Resources Director, and Mr. Mark Altaha, Historic Preservation Officer, for permission to access and help collecting turquoise from the
mines at Canyon Creek. Sample collection was also assisted by Ryan Mathur and Saul Hedquist. This project was helped and improved through interactions with many people, including Barbara Mills, Joan Mathien, Spence Titley, Saul Hedquist, Sharon Hull, and Mostafa Fayek.

References


Blake, W.P., 1858, The chalchihuitle of the ancient Mexicans: Its locality and


Johnson, C.M., and Lipman, P.W., 1990, H, O, Sr, Nd, and Pb isotope geochemistry of the Latir Volcanic Field and cogenetic intrusions, New Mexico, and relations


Thibodeau, A.M, Killick, D.J., Ruiz, J., Chesley, J.T., Deagan, K., Cruxent, J., Lyman, W., 2007, The strange case of the earliest silver extraction by European Colonist in


Weigand, P.C., 1994, Observations on ancient mining within the northwestern regions of the Mesoamerican civilization, with emphasis on turquoise, in Craig, A.K. and West,


Table 1. Summary of turquoise source areas discussed in text, their locations, and evidence for Prehispanic mining

<table>
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<tr>
<th>Turquoise Source Areas</th>
<th>County and State</th>
<th>Associated Geographic Feature</th>
<th>Prehispanic Mining?</th>
<th>Selected References</th>
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<td>1b. Turquoise Mountain</td>
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<tr>
<td>3. Crescent Peak District</td>
<td>Clark County, NV</td>
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<td>Yes</td>
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<td>5. Gleeson District</td>
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<td>Weigand and Harbottle (1993)</td>
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<td>6. Courtland District</td>
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<td>Dragoon Mountains</td>
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<td>7. Silver Bell District</td>
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<td>Jarilla Mountains</td>
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<td>Modreski and Murphy (2002)</td>
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<td>17. Canyon Creek</td>
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Table 2. Lead and strontium isotopic ratios of turquoise in the Southwest United States

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**Gleeson District**

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**Courtland District**

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R, Repeat Measurement
Figure 1. Map of turquoise source areas discussed in this study. Circles represent source areas where turquoise has $^{87}\text{Sr}/^{86}\text{Sr}$ ratios greater than 0.710. Squares represent source areas where turquoise has $^{87}\text{Sr}/^{86}\text{Sr}$ ratios less than 0.710. Turquoise sources are broken down into three primary groupings. Coloring of the map samples reflect these groupings and indicate source areas that are discussed as a group in the text. Turquoise from Canyon Creek and the Royston district are each discussed separately in the text based on their distinctive geologic settings. Dashed lines indicate approximate locations of the boundaries between Pb isotope provinces in Arizona (the Mojave, Central Arizona and Southeastern Arizona Provinces) as defined by Wooden at al. (1988), Wooden and Miller (1990) and Wooden and Dewitt (1991). Sub-boundary in the Southeastern Arizona Province (SEAZ) is drawn as defined by Bouse et al. (1999) and separates the northern Southeastern Arizona Province (nSEAZ) from the southern Southeastern Arizona Province (sSEAZ). The Central Arizona and Southeastern Arizona Provinces are broadly correlative with the Yavapai and Mazatzal Provinces defined tectonostratigraphically by other workers (e.g., Bowring and Karlstrom, 1990).
Figure 2. $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of all samples investigated for this study by source area. Color of symbols and groupings are consistent with Figure 1. All data points are larger than the 2σ external error.
Figure 3. Lead isotopic ratios of turquoise and sulfides from the Mineral Park District and outcropping Proterozoic rocks from the Cerbat Range. Three areas of turquoise mineralization in the Mineral Park district are represented: Ithaca Peak, Turquoise Mountain, and a third (unnamed) locality. Data on sulfides is from Bouse et al. (1999) and data on Proterozoic rocks is from Wooden and DeWitt (1991). 1.7 Ga isochron passes through the estimated initial lead isotopic composition of the Mojave Province: \( \frac{206}{204} \text{Pb} = 16.1, \frac{207}{204} \text{Pb} = 15.38, \frac{208}{204} \text{Pb} = 35.65 \) (Wooden and DeWitt, 1991). All data points are larger than the 2σ external error.
Figure 4. Comparison between turquoise source areas in Group 1: Mineral Park district, Halloran Springs district, and Crescent Peak. Data on sulfides from the Mineral Park district and Proterozoic rocks from the Cerbat Mountains are shown for reference (Bouse et al., 1999; Wooden and DeWitt, 1991). Mojave isochron is shown as drawn in Figure 3. All data points are larger than the 2σ external error.
Figure 5. Plot comparing the lead isotopic signature of turquoise from deposits in the Mojave Province (Group 1) with turquoise from Southeastern Arizona Province (Group 2). All data points shown have $^{87}\text{Sr}/^{86}\text{Sr}$ ratios $> 0.710$. Turquoise from sources within the Mojave province generally have higher and more variable $^{208}\text{Pb}/^{204}\text{Pb}$ ratios for a given $^{206}\text{Pb}/^{204}\text{Pb}$ as well as higher $^{207}\text{Pb}/^{204}\text{Pb}$ ratios for a given $^{206}\text{Pb}/^{204}\text{Pb}$. These isotopic characteristics are consistent with the unique initial lead isotopic composition, relatively low $\mu$, and high/variable $\kappa$ values inferred for the Mojave Basement (Wooden and Dewitt, 1991). Conversely, turquoise in the Southeastern Arizona Province is readily distinguished from Mojave Province turquoise by generally lower $^{208}\text{Pb}/^{204}\text{Pb}$ ratios, lower $^{207}\text{Pb}/^{204}\text{Pb}$ ratios for a given $^{206}\text{Pb}/^{204}\text{Pb}$, and higher $^{206}\text{Pb}/^{204}\text{Pb}$. All data points are larger than the $2\sigma$ external error.
Figure 6. Lead isotopic ratios of turquoise source areas within Group 2 compared with the lead isotopic ratios of sulfide mineralization from Laramide copper deposits in the SEAZ. Sulfides and turquoise have been assigned to either the northern SEAZ Province (nSEAZ) or southern SEAZ Province (sSEAZ) based on Bouse et al. (1999). Data on turquoise from the Silver Bell district is from Thibodeau et al. (in press). See text for discussion of sample T3.
Figure 7. $^{207}\text{Pb}/^{204}\text{Pb}$ vs. $^{208}\text{Pb}/^{204}\text{Pb}$ plot of turquoise source areas within Group 3 and the Royston district. All samples shown have $^{87}\text{Sr}/^{86}\text{Sr}$ ratios less than 0.710. We plot this data using an unusual pair of axes because it offers the best visual representation of the isotopic differences among these source areas. ($^{206}\text{Pb}/^{204}\text{Pb}$ ratios are less diagnostic of these source areas than either $^{207}\text{Pb}/^{204}\text{Pb}$ or $^{208}\text{Pb}/^{204}\text{Pb}$.) Note that turquoise from the Cerrillos source area splits into two distinct groupings, one containing samples from Mt. Chalchihuitl, and the other containing turquoise samples from Turquoise Hill (see text for details). All data points are larger than the 2σ external error.
Figure 8. Comparison of lead isotopic ratios of turquoise within Groups 1, 2, and 3, plus turquoise from Canyon Creek and the Royston district. Samples depicted by solid triangles have $^{87}\text{Sr}/^{86}\text{Sr}$ ratios $> 0.710$, while samples depicted by open circles have $^{87}\text{Sr}/^{86}\text{Sr}$ ratios $< 0.710$. Note that turquoise from deposits in central New Mexico and southern Colorado (Group 3) have similar lead isotopic signatures to turquoise from the Southeastern Arizona Province (Group 2), but distinct strontium isotopic signatures. Some mines and source areas with distinct isotopic signatures are indicated. All data points are larger than the 2σ external errors.
HIGH PRECISION ISOTOPIC ANALYSES OF LEAD ORES FROM NEW MEXICO BY MC-ICP-MS: IMPLICATIONS FOR TRACING THE PRODUCTION AND EXCHANGE OF PUEBLO IV GLAZE-DECORATED POTTERY

Submitted to the Journal of Archaeological Science
HIGH PRECISION ISOTOPIC ANALYSES OF LEAD ORES FROM NEW MEXICO BY MC-ICP-MS: IMPLICATIONS FOR TRACING THE PRODUCTION AND EXCHANGE OF PUEBLO IV GLAZE-DECORATED POTTERY

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Abstract

Between ca.1275 and 1700 C.E., Pueblo groups in the northern Southwest United States produced and exchanged ceramic bowls decorated with lead-based glaze-paints. Previous studies of these glaze-decorated bowls have used lead isotopic analysis by ICP-MS to identify the sources of lead used by Pueblo potters, and investigate how social or economic factors may have influenced resource use among different Pueblo communities (e.g. Habicht-Mauche et al., 2000, 2002; Huntley et al., 2007; Huntley 2008). However, interpretations of much of this isotopic data have remained provisional because of overlap among the isotopic ratios of potential sources and because the isotopic composition of many glaze paints do not clearly match any known source. Here, we use multi-collector ICP-MS to re-measure the lead isotopic composition of 46 samples of lead sulfide (galena) and lead carbonate (cerussite) from sources in New Mexico that were potentially utilized by Pueblo potters, including mines within the Cerrillos Hills, Magdalena, Hansonburg, and Joyita Hills mining districts. These results define the
isotopic composition of lead ores from these districts with greater precision and accuracy than achieved in previous studies, and better distinguish among these mining districts in lead isotope space. Most significantly, we find that galena mineralization within the Cerrillos Hills only has a modest degree of isotopic variation, with \(^{206}\text{Pb}/^{204}\text{Pb}\) ratios from 18.508 to 18.753, \(^{207}\text{Pb}/^{204}\text{Pb}\) ratios from 15.580 to 15.608, and \(^{208}\text{Pb}/^{204}\text{Pb}\) ratios from 38.388 to 38.560. This range is far narrower than previously reported, and should supersede previously published values for this district. In total, we conclude that isotopic measurements of both ores and glaze paints made by MC-ICP-MS will provide new information about the provenance of lead in glaze paints and allow for more detailed interpretations about resource procurement and exchange in the Pueblo world.

1. Introduction

Glaze-decorated ceramics were both produced and widely exchanged by Pueblo groups in the Southwest United States (U.S.) between \(~1275\) and \(~1700\) CE. Lead (Pb), an effective flux which lowers the melting points of silica and alumina, is a major component of many glaze decorations, often present at concentrations of at least 35-50% by weight (Habicht-Mauche et al., 2000; Huntley et al., 2007; Huntley, 2008).

Since 2000, lead isotopic measurements of glazes have been employed to infer the source of lead ore used by Pueblo potters in the Galisteo Basin (Habicht-Mauche et al., 2000; 2002; Nelson and Habicht-Mauche, 2006), Salinas area (Huntley et al., 2007) and Zuni region (Huntley, 2008) of New Mexico (Fig. 1). Determining the source of raw materials used by Pueblo potters provides information about the interactions between
communities that produced glaze wares across eastern Arizona and New Mexico, and the social and economic patterns that influenced resource use. Isotopic comparisons of glaze paints and ores indicate that certain mining districts, such as those located in the Cerrillos Hills and Magdalena Mountains, may have been particularly important to Pueblo potters. (Fig. 1, Habicht-Mauche et al., 2000; 2002; Huntley et al., 2007; Huntley, 2008). However, interpretations of lead procurement remain provisional because published isotopic ratios of glaze samples often do not precisely match the previously published ratios of any of the potential ore sources, or cannot be clearly assigned to a single source (Huntley et al., 2007; Huntley, 2008). These uncertainties have been attributed to (a) the prehistoric use of ore sources which have not yet been characterized with lead isotopes, (b) the mixing of ores from different sources to make glazes, and (c) isotopic overlap among the ore sources.

The advent of multi-collector inductively coupled mass spectrometry (MC-ICP-MS) in the late 1990’s now makes it possible to routinely generate high precision measurements of lead isotopic ratios. However, this technique has never been applied to measure the isotopic composition of either lead ore from the potential sources used by Pueblo potters, or lead-rich glazes found on Pueblo IV ceramics. Our goal in this paper is to demonstrate that high-precision lead isotopic measurements can provide much tighter clusters of isotopic ratios for lead sources than were achieved by earlier techniques.

In the present study, we use MC-ICP-MS to re-measure the lead isotopic composition of galena (PbS) and cerussite (PbCO₃) from the Cerrillos Hills, Hansonburg, Joyita Hills, and Magdalena districts in New Mexico (Fig. 1). All these areas are
considered to be possible sources of lead ores used by potters in the Galisteo, Salinas, and Zuni Pueblos (Habicht-Mauche et al., 2000; 2002; Huntley et al., 2007; Huntley, 2008). Among these areas, we place particular emphasis on characterizing ores from the Cerrillos Hills because of the district’s established importance as a site of ancient lead and turquoise mining in the Southwest U.S. (Schroeder, 1979; Warren and Weber, 1979; Warren and Mathien, 1985; Mathien, 1998; Bice et al., 2003).

We compare our results using MC-ICP-MS to isotopic measurements that have been made on the same ore deposits using single-collector ICP-MS (Habicht-Mauche et al., 2000; 2002; Huntley et al., 2007) and thermal ionization mass spectrometry (TIMS) (Ewing, 1979; Habicht-Mauche et al., 2002; Stacey and Hedlund, 1983). These new measurements, which are made on the same samples used by Habicht-Mauche et al. (2000), Habicht-Mauche et al. (2002), and Huntley et al. (2007), allow us to (a) narrow the range of lead isotopic ratios associated with these ore deposits, (b) re-visit questions of isotopic overlap among sources and (c) consider how regional geologic controls influence the isotopic signature of lead ores across these regions of New Mexico and thus impact studies of lead provenance. The results indicate that high-precision lead isotopic measurements are likely to both simplify and revise interpretations about the source of lead used to create glaze-decorated ceramics, and thus advance our knowledge of interaction and exchange among Pueblo communities in the Pueblo IV and protohistoric Southwest.

2. Advantages of MC-ICP-MS
Isotopic ratios of lead in archaeological materials were first measured by TIMS (Brill and Wampler, 1967; Gale and Stos-Gale, 1982), but the technique requires laborious and expensive sample preparation and offers relatively low sample throughput. Single collector ICP-MS was developed in the 1980s and 1990s (Vanhaecke et al., 2009) and presented a quicker and lower cost alternative for isotopic determinations. Previous studies of lead provenance in southwestern glaze paints have relied upon the determination of isotope ratios of both glazes and ores by solution analyses via single collector magnetic sector high-resolution (Hr)-ICP-MS.

While single-collector ICP-MS has advantages over conventional TIMS measurements in terms of both the cost and efficiency of lead isotope analysis, the precision of the analyses is worse (Vanhaecke et al., 2009). Habicht-Mauche et al. (2002) demonstrate the limitations of the Hr-ICP-MS dataset on ores from New Mexico by comparing the lead isotopic ratios of three ore samples (all from the Mina del Tiro mine, in the Cerrillos Hills) measured using three different techniques: acid dissolution Hr-ICP-MS, laser ablation (LA)-ICP-MS, and TIMS. Of these analyses, the measurements made by TIMS have the least scatter and the most accurate representation of the true isotopic signature of ore from the Mina del Tiro mine (Fig. 2). The ratios measured by Hr-ICP-MS on the same samples (using both laser ablation and acid dissolution) are both more variable than the TIMS values, and offset from them in different directions (Fig. 2). The offsets of these measurements can be attributed to uncorrected mass discrimination during Hr-ICP-MS analysis (Habicht-Mauche et al., 2002). In contrast, our analyses of Mina del Tiro galena samples by MC-ICP-MS agree well with the TIMS values, and are
the most precise (Fig. 2). In the past decade, MC-ICP-MS has become the choice for measurement of lead isotope ratios for geological, and more recently, archaeological applications (Balcaen et al., 2010). For the measurement of lead isotopic ratios, it exceeds the precision of conventional TIMS measurements, offers rapid analysis, and, in some cases, requires minimal sample preparation (e.g. Baker et al., 2006 and this study).

Lead isotopic measurements made by MC-ICP-MS are more precise than those made using single collector ICP-MS and conventional TIMS techniques primarily because an ICP source combined with a multi-collector array makes it possible to use an external element (in this case, thallium) to internally correct for mass discrimination during analysis (Rehkamper and Halliday, 1998; Rehkämper and Mezger, 2000; White et al., 2000; Woodhead, 2002). Furthermore, MC-ICP-MS improves upon single-collector ICP-MS because it allows for the simultaneous measurement of signals, and thus the isotopic ratios are not affected by fluctuations in the ICP source. High precision lead isotopic measurements made by MC-ICP-MS provide more precise data on the isotopic composition of both ores and glazes and thus should ultimately facilitate better interpretations of lead provenance in Pueblo glaze paints.

3. Archaeological context for study

Not much is directly known about the potential sources of lead ore utilized by Pueblo potters because there is little archaeological evidence of Prehispanic lead mining in the relevant areas of New Mexico or eastern Arizona. One major exception, however, is the Cerrillos district, where physical evidence of lead mining by Pueblo groups has been recognized for centuries and is well documented historically (see Mathien, 1998 for
summary). Archaeological excavations of the Mina del Tiro and Bethsheba mines within the Cerrillos Hills have revealed sherds and tools that demonstrate that these lead deposits there were exploited between ca. 1300 and ca. 1700 CE (Bice et al., 2003; Warren and Weber, 1979).

However, given that glaze technology probably spread around the turn of the fourteenth century from the upper Little Colorado, Zuni and possibly Acoma regions in the Western Pueblo region to Eastern Pueblo communities along the northern and southern Rio Grande, it is likely that the Cerrillos district was not the only source of lead supplying Pueblo potters. For example, along the southern Rio Grande, there are large historic and late prehistoric Pueblo settlements (Abó, Quarai) that either produced glaze-decorated ceramics (Huntley et al., 2007) or that appear to have had relationships with communities that produced glaze wares (Huntley, 2008). Although evidence for ancient lead mining in the area is sparse, some ore deposits in this region, such those of the Magdalena Mountains, Joyita Hills, and Oscura Mountains are considered potential sources of lead minerals because of their proximity to these settlements (Huntley et al., 2007). Furthermore, there is some documentary evidence to suggest that ores of the Oscura Mountains (Hansonburg district) were mined by Pueblo groups before the arrival of the Spanish (Taggart et al., 1989) and the presence of stone hammers has been recorded on outcrops in this district (Eveleth, 2002). It is possible that subsequent Spanish and American mining activities have eliminated traces of earlier Pueblo quarries in some locales. In this light, lead isotopes become particularly important tools in the
study of glaze paint production because they provide empirical constraints on the sources of lead used by Pueblo groups, when other lines of evidence are absent.

4. Geological contexts of ore deposits

The Cerrillos Hills are about 20 miles southwest of Santa Fe and are part of the Ortiz Porphyry Belt, a 25-mile long north-south trending belt of Oligocene igneous rocks in northern New Mexico (Maynard et al., 1991). Within the Cerrillos district, veins containing galena, pyrite, sphalerite, and chalcopyrite are primarily found in heavily fractured monzonite and andesite porphyry stocks. These ore minerals were deposited by hydrothermal fluids after the emplacement and solidification of the youngest plutons in the igneous complex (Disbrow and Stoll, 1957).

The lead deposits in the Magdalena district lie to the west of the Rio Grande on the western flank of the northern Magdalena Mountains. They are considered to be volcanic-epithermal in origin and are part of a suite of carbonate-hosted lead-zinc deposits formed by replacement of Paleozoic carbonates, which occur throughout southwestern New Mexico (McLemore, 2001). Most deposits of lead ore in the Magdalena district are stratabound and extend from the contact of the Kelly limestone with Tertiary igneous rocks in the north, along a north-south trend that is parallel to the major faulting in the district (Titley, 1959).

The mining districts of the Joyita Hills and Oscura Mountains (the Hansonburg district) primarily contain deposits of barite, fluorite, and galena (Lasky, 1932) and such deposits are prevalent along the eastern margin of the Rio Grande Rift (McLemore, 2001). In the Hansonburg district, ore minerals fill fissures and fault breccia cavities in
Paleozoic carbonates, while in the Joyita Hills, they fill fissures in Proterozoic granites and cavities in Paleozoic limestones (McLemore, 2001). These deposits were formed by low-temperature brines that were expelled during compaction of sedimentary rocks in surrounding continental basins. As they circulated by heat convection, these brines leached metals from the surrounding country rock (McLemore, 2001). Rio Grande Rift barite-fluorite-galena deposits are similar in origin to Mississippi Valley Type deposits in the central U.S. (Goldhaber et al., 1995), and have already been shown to have radiogenic lead isotopic compositions that reflect the interaction of the ore-forming fluids with upper crustal rocks (Ewing, 1979; Stacey and Hedlund, 1983).

5. Materials and methods

To re-evaluate the lead isotopic composition of lead ores from the Cerrillos Hills, one of us (AMT) re-measured the isotopic ratios of a total of 32 galena samples from 11 individual mines. Galena samples from the Cerrillos mining district derive from the same collection of samples analyzed by Habicht-Mauche et al. (2000, 2002) and Huntley et al. (2007). Care was taken to select samples from mines that represent the full range of isotopic compositions previously reported for Cerrillos ores (Habicht-Mauche et al., 2002). In addition to samples from the Cerrillos Hills, we also analyzed 14 specimens of galena and cerussite from the Magdalena, Hansonburg and Joyita Hills mining districts in Socorro County, New Mexico. The analyzed mineral specimens from Socorro County were selected from collections curated by the Mineral Museum at the New Mexico Bureau of Geology and Mineral Resources (Socorro, New Mexico), and are a subset of the samples used by Huntley et al. (2007) to interpret sources of lead used by potters in
the Salinas Pueblos. Unfortunately, not all of the samples measured for Huntley et al. (2007) were still present in the museum’s collection in 2009, and thus this MC-ICP-MS dataset is not as large as the one previously determined by Hr-ICP-MS. All samples are described in Table 1.

Instead of dissolving small fragments of galena and cerussite, polyester-tipped clean-room swabs dipped in clean 2% nitric acid (prepared from MQ water and twice distilled acid) were used to remove lead from the surface of each sample. This method takes away much of the labor and cost associated with sample dissolution and separation of lead via ion exchange chemistry, and is justified by the relatively pure nature of the lead ores. The procedure used to swab the samples was comparable to that described in Thibodeau et al. (2012) for objects made of lead metal. To empirically demonstrate the validity of using this technique to remove lead from the surface of these mineral specimens, we compare this data with fully dissolved galena crystals from the J.A. Logan mine in the Cerrillos Hills. Samples C-27 and C-28 were dissolved in acid-cleaned Savillex vials with concentrated twice-distilled nitric acid. After dissolution, lead was separated from each sample using Sr resin (Eichrom Industries). All samples were diluted to concentrations of ~50 ppb before analysis.

Solutions were analyzed using a GV-instruments MC-ICP-MS at the University of Arizona, over the course of four analytical sessions between July of 2009 and October of 2010. The details of the analysis and data reduction are described by Thibodeau et al. (2012) and Thibodeau et al. (2007). The absolute values of the 2σ errors associated with the measurements of the NBS-981 standard range from ±0.0038-0.0091 for $^{206}\text{Pb}/^{204}\text{Pb}$,
±0.0035- .0.0074 for \(^{207}\text{Pb}/^{204}\text{Pb}\), and ±0.010-0.018 for \(^{208}\text{Pb}/^{204}\text{Pb}\). These are the external errors associated with the measurements in Table 1 and referred to in the Figures below.

6. Results and discussion

6.1 Isotopic fingerprints

To be consistent with previous presentations of lead ore and glaze paint data from New Mexico, and for reasons eloquently articulated by Albarède et al. (2011), we discuss this data in terms of the ratios traditionally used in isotope geology: \(^{206}\text{Pb}/^{204}\text{Pb}\), \(^{207}\text{Pb}/^{204}\text{Pb}\), \(^{208}\text{Pb}/^{204}\text{Pb}\). In the present study, isotopic ratios of galena from the Cerrillos Hills span a limited range of values: \(^{206}\text{Pb}/^{204}\text{Pb}\) ratios vary between 18.508-18.753, \(^{208}\text{Pb}/^{204}\text{Pb}\) ratios vary between 38.388 -38.560, and \(^{207}\text{Pb}/^{204}\text{Pb}\) ratios vary between 15.580-15.608 (Table 1; Fig. 3). The isotopic ratios of the two samples prepared using dissolution and ion-exchange chromatography (C-27 and C-28) are consistent with other isotopic measurements of samples prepared by our swabbing technique from the same mine (Table 1). When compared to previously published data on these ores (Habicht-Mauche et al., 2002), the isotopic ratios re-measured by MC-ICP-MS fall within a much narrower range of ratios and define significantly different linear trends on bivariate plots (Fig. 3). The consistency of the isotopic signature from mines across the Cerrillos district suggests to us a common geological source for the lead in ores across the district, despite differences in the mineralogy and orientation of the lead-zinc veins. Notably, the variation in \(^{207}\text{Pb}/^{204}\text{Pb}\) ratios of these ores barely exceeds the 2σ analytical error associated with the measurements. Furthermore, this new dataset reveals no systematic isotopic differences between mines located in the northern and southern parts of the
district, as has previously been suggested (Habicht-Mauche et al., 2000; 2002; Huntley et al., 2007). Thus, for purpose of interpreting the provenance of archaeological materials, all the lead mines of the Cerrillos Hills should be considered a single source.

There is good isotopic separation among the ore deposits investigated from southwestern New Mexico, where the isotopic ratios measured using MC-ICP-MS reveal a more restricted range of values for individual deposits compared to previous ICP-MS measurements (Fig 4). Isotopic analyses via TIMS of galena from these districts have also been reported in the geological literature by Stacey and Hedlund (1983) and Ewing (1979), and for comparative purposes, we include some of these published values in Table 1. Overall, the data we report here for deposits from Socorro County are coherent with previously published TIMS values for galena in these same mining districts.

Ores from the Hansonburg district have most radiogenic signature of all ores considered in this study, with $^{206}\text{Pb}/^{204}\text{Pb} > 22.0$, $^{207}\text{Pb}/^{204}\text{Pb}$ values $> 15.9$, and $^{208}\text{Pb}/^{204}\text{Pb}$ values $> 40.1$. Galena from the Joyita Hills is slightly less radiogenic than ores from the Hansonburg district, and the one sample included in this study has $^{206}\text{Pb}/^{204}\text{Pb} = 20.95$, $^{207}\text{Pb}/^{204}\text{Pb} = 15.81$, and $^{208}\text{Pb}/^{204}\text{Pb} = 40.50$. This data point plots on the extension of a line formed by Hansonburg samples on a $^{206}\text{Pb}/^{204}\text{Pb}$ vs. $^{207}\text{Pb}/^{204}\text{Pb}$ graph. The radiogenic signature of lead ores in both of these deposits reflects the derivation of lead from upper crustal sources, consistent with their geologic setting. Four samples from the Magdalena district are much less radiogenic than either the Hansonburg or Joyita Hills samples, and have similar isotopic ratios to ores from the Cerrillos Hills. In this study, samples from Magdalena have the following range of lead isotope ratios:
$^{206}\text{Pb}/^{204}\text{Pb} = 18.26-18.53$, $^{207}\text{Pb}/^{204}\text{Pb} = 15.56-15.62$, $^{208}\text{Pb}/^{204}\text{Pb} = 38.08-38.40$. While these samples form an array on a $^{206}\text{Pb}/^{204}\text{Pb}$ v. $^{208}\text{Pb}/^{204}\text{Pb}$ plot, they scatter on $^{206}\text{Pb}/^{204}\text{Pb}$ vs. $^{207}\text{Pb}/^{204}\text{Pb}$ (Fig. 5). One sample from Stacey and Hedlund (1983) clusters with these samples, while a second from the Linchburg mine (Titley, 1961), has a slightly more radiogenic value.

One obstacle to clear interpretations of lead isotopic ratios in glaze paints has been the apparent overlap among the isotopic signatures of ores from the Cerrillos, Hansonburg, Magdalena districts in previous ICP-MS datasets (Huntley et al., 2007; Huntley, 2008). A primary goal of this study is to reassess such overlap with high precision measurements. Before doing so, however, it is important to acknowledge an important caveat: all lead ores sampled from deposits in the Socorro vicinity (Magdalena, Hansonburg, the Joyita Hills) are part of museum collections, and there is no way to verify that each sample is attributed to the correct source. For example, one sample from Hansonburg (H-9) analyzed for this study and also reported by Huntley et al. (2007) has an isotopic ratio that is far offset from the other Hansonburg samples (see Fig. 4 and Table 1, this study and Fig. 3 in Huntley et al., 2007). Such a substantial variation within common lead ores from the same district would be extremely unusual, and because this sample derives from a museum collection, there is no way to verify its collection locale or true origin. Additional reasons for skepticism include the fact that no other published isotopic data from Hansonburg reveals a corresponding or similar isotopic ratio (Stacey and Hedlund 1983; Ewing 1979), and there is no geological evidence for multiple types of lead mineralization in the district (McLemore, 2001). We thus believe it is fair to regard...
the provenance of H-9 with skepticism, and while we include this measurement in our table, we do not consider it in our interpretation of source “fingerprints.”

Likewise, we also note that two samples associated with the Magdalena district and reported in Huntley et al. (2007) and Huntley (2008) are offset from the main cluster of samples attributed to Magdalena and greatly expand the isotopic fingerprint of ores from the district. As with Hansonburg, we are reluctant to accept these outliers as representative of lead ores from Magdalena. The caution is justified, as we were able to reanalyze one of these samples (M-2) and could not reproduce the previously reported isotopic signature for this sample. Instead, this new measurement clusters with isotopic ratios of other samples from the Magdalena district (Fig. 4). It thus appears the previously reported ratios for this sample are in error and should be disregarded. Although we were unable to reanalyze the second outlying sample, this first measurement provides sufficient cause to suspect that the other may also represent an erroneous measurement, or possibly, as we argue in the case of H-9, a mislabeled sample. Our goal is not to simply explain away inconvenient data, but instead to critically consider alternative reasons that measurements may deviate significantly from expectation. In both these cases, we believe there is adequate reason to reject the outlying measurements from the Hansonburg and Magdalena districts.

Thus, the new dataset we present here resolves much of the overlap previously reported among the Magdalena, Cerrillos, and Hansonburg districts, and provides a more precise isotopic characterization of each source (Fig. 5). Only ores from the Magdalena and Cerrillos districts appear to have overlapping isotopic signatures (Fig. 5). Despite this
overlap, we note that lead ores from the Magdalena district tend to have lower $^{208}\text{Pb}/^{204}\text{Pb}$ values than galena in the Cerrillos Hills and do not form a strong linear trend on a $^{206}\text{Pb}/^{204}\text{Pb}$ vs. $^{207}\text{Pb}/^{204}\text{Pb}$ plot. However, the scatter of the data points suggest to us that more samples are needed to fully characterize the range of isotopic compositions in ores from the Magdalena district. Thus, we cannot ascertain the full extent of the overlap between the signatures of ores from the Magdalena Mountains and Cerrillos Hills. We note, however, that Magdalena and Cerrillos appear to be characterized by distinct ranges of isotopic ratios, and remain optimistic that the distinction between these sources will be visible in high precision isotopic data generated on glaze paints. This confidence also derives from our observation that that lead ores from the Cerrillos Hills have a very narrow range of isotopic ratios. Such specificity should allow high precision isotopic measurements to readily distinguish between glazes that are made from Cerrillos ores and glazes that are made from ores mined outside of the Cerrillos district.

6.2 Isotopic trends

One of this study’s most significant findings is the observation that ores from the Cerrillos Hills and ores from southwestern New Mexico form similar trends on bivariate plots, particularly in $^{206}\text{Pb}/^{204}\text{Pb}$ vs. $^{207}\text{Pb}/^{204}\text{Pb}$ space (Fig. 6). This finding is in contrast to previous characterizations of ores from northern and southern New Mexico, which showed the isotopic ratios of galena from the Cerrillos Hills extending along a significantly different trend than ores from southwestern and south-central New Mexico (Huntley et al., 2007). The similarity of the two trends in this study results from the significant revision these new data make to the lead isotopic signature of galena from the
Cerrillos Hills and the significantly flatter array formed by these ratios measured by MC-ICP-MS in both $^{206}\text{Pb}/^{204}\text{Pb}$ vs. $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{206}\text{Pb}/^{204}\text{Pb}$ vs. $^{208}\text{Pb}/^{204}\text{Pb}$ space. Furthermore, the restricted range of isotopic ratios associated with Cerrillos ores in this new dataset indicates that as a single source, the trend formed by these ores does not extend very far, particularly compared to the trend formed by data collected on galena from multiple of deposits across southwestern New Mexico.

The deposits considered in the paper may represent a fraction of the deposits that could have been utilized in prehistory, and it is thus relevant to consider the isotopic signature of these ores from a regional geological perspective. The linear array formed by ore samples from southwestern New Mexico on a $^{206}\text{Pb}/^{204}\text{Pb}$ vs. $^{207}\text{Pb}/^{204}\text{Pb}$ plot was both reported and explained by Stacey and Hedlund (1983) who used TIMS to characterize the isotopic composition of lead-mineralization and associated igneous rocks from across the region. Because their isotopic data on lead ores include samples from Magdalena, Hansonburg, and the Joyita Hills, we compare their full dataset on lead ores with ours in Figure 6. Stacey and Hedlund (1983) infer the linear array formed by these ores on a $^{206}\text{Pb}/^{204}\text{Pb}$ vs. $^{207}\text{Pb}/^{204}\text{Pb}$ plot reflects the inheritance of ore lead from crustal sources that evolved from basement rocks of similar age and initial lead isotopic compositions. Furthermore, a regression line through this data can be interpreted as secondary isochron with an approximate age of 1.5 Ga (Stacey and Hedlund, 1983). This age is consistent with observations that much of New Mexico and adjacent areas of Arizona are underlain by Proterozoic rocks of the Mazatzal Province, which largely formed between 1.4-1.7 billion years ago and are inferred to share isotopic similarities.
(Karlstrom et al., 2004). Thus, the findings of Stacey and Hedlund (1983) indicate that, despite many different styles of mineralization, isotopic ratios of lead ores from southwestern New Mexico would be expected to roughly fall along this array in $^{206}\text{Pb}/^{204}\text{Pb}$ vs. $^{207}\text{Pb}/^{204}\text{Pb}$ space. This expectation is supported by earlier measurements of lead ore from deposits in south-central New Mexico by Ewing (1979), which both fall along and extend the trend formed by the data of Stacey and Hedlund (1983). Because of the linearity of this data from various ore deposits in $^{206}\text{Pb}/^{204}\text{Pb}$ vs. $^{207}\text{Pb}/^{204}\text{Pb}$ space, this plot may not permit clear evaluation of glaze paints if they have isotopic compositions that fall along this array, but do not match a specific source. Plausibly, such an intermediate composition could either represent mixing of known sources or the use of an uncharacterized ore deposit. Fortunately, the data do not fall along a single array in $^{206}\text{Pb}/^{204}\text{Pb}$ vs. $^{208}\text{Pb}/^{204}\text{Pb}$ space, and as discussed in Section 5, it may be possible to detect mixtures of lead from different sources.

The array formed by the isotopic ratios of ores from the Cerrillos Hills can be interpreted in a similar manner. When plotted on a $^{206}\text{Pb}/^{204}\text{Pb}$ v. $^{207}\text{Pb}/^{204}\text{Pb}$ graph, we interpret the data collected on Cerrillos samples as a secondary isochron that yields a model age of roughly 1.7 Ga (Fig. 6). This age is consistent with the position of the district within a transition zone that separates basement rock of the Mazatzal Province (post-1.7 Ga crust) from those of the older Yavapai Province (pre-1.7 Ga crust). Thus, these results indicate that the lead in ore deposits of the Cerrillos Hills was likely inherited from crustal sources that evolved from Precambrian basement rocks and accurately reflect their position near the northernmost extent of Mazatzal basement.
Although the Cerrillos samples and samples from southern New Mexico fall along slightly different trends (as reflected in the distinct ages given by secondary isochrons), the very restricted range of ratios found on ores from Cerrillos suggests that trends alone will likely not be useful in distinguishing between lead from the Cerrillos district and lead from more southern ore sources. However, by placing these analyses in a geologic context, we hope to demonstrate that variation in these ores is not random, but is patterned according the geological backgrounds of the deposits.

7. Conclusions and implications for future research

These measurements are the first high-precision analyses of lead ores from New Mexico and have significant archaeological and archaeometric implications for the study of glaze wares across southwestern U.S. As MC-ICP-MS facilities become more readily available and allow other researchers to take advantage of this rapid and precise methodology, this dataset should prove useful toward the study of production and exchange of glaze wares among Pueblo communities.

The most significant finding of this study is the substantial revision of the isotopic fingerprint of lead ores from the Cerrillos Hills. Not only does this new data reduce the isotopic variation within the district by an order of magnitude, it shows the slope of the trend formed by Cerrillos ores on bivariate plots to be considerably different than previously reported. We also suggest that previous observations of isotopic overlap among some of the ores sources (i.e. the Cerrillos, Hansonburg, and Magdalena districts) can be largely attributed to mislabeled museum samples and erroneous isotopic measurements. The only overlapping sources recognized by this study are the Magdalena
and Cerrillos districts. However, the Cerrillos district remains the only locale with extensive archaeological evidence for Prehispanic mining of lead ores, and the extremely narrow range of isotopic ratios associated with Cerrillos ores should make it possible to assess the extent to which these ores were or were not used in the making of glaze ware in the Pueblo world. Future work should include further sampling and analysis of lead ore from other sources across New Mexico (especially in the Socorro area), and the generation of new MC-ICP-MS data on previously measured glazes, so that they are directly comparable to the values represented here.

A potentially significant outcome of applying high precision isotopic measurements to questions of glaze paint provenance could be the clearer evaluation of the possibility that Pueblo potters mixed ores derived from different sources. The lead isotope system is particularly well suited for evaluating mixing, because two and three-component mixtures form lines on bivariate plots and planes in three-dimensional space. Mixing is most effectively evaluated in plots that utilize $\text{Pb}^{206}/\text{Pb}^{204}$, $\text{Pb}^{207}/\text{Pb}^{204}$ and, $\text{Pb}^{208}/\text{Pb}^{204}$ ratios and thus is best assessed with high-precision measurements (Ellam, 2010). Furthermore, evaluating mixing in glazes should be relatively straightforward, because unlike archaeological metals or glass objects, their signatures do not have the potential to be influenced by multiple episodes of recycling. Therefore, if glazes represent two or three component mixtures, it may possible to identify the sources of the lead involved, which would greatly enhance interpretations of lead procurement.

Because interpretations of ore procurement rely heavily on lead isotope data, determining precise isotopic fingerprints for potential sources will ultimately lead to
more robust constraints on our knowledge of lead procurement, use, and exchange in the Pueblo world. These results suggest that further study of glaze paints using MC-ICP-MS has the potential to clarify interpretations of lead provenance and provide novel insights into the manufacture and exchange of glaze-decorated ceramics in the Pueblo Southwest over the four centuries of their production.

Acknowledgments

We thank Mark Baker for his invaluable help in the lab. We also thank Virgil Lueth and the Mineral Museum at the New Mexico Bureau of Geology and Mineral Resources (New Mexico Institute of Technology) for access to samples from the Socorro area. This research was supported by NSF grant BCS-0852270. David Killick commented on earlier drafts of this manuscript, and greatly improved its final content. Thank you to Saul Hedquist for assistance with Figure 1.

References


Taggart, J.E., Rosenzweig, A., Foord, E.E., 1989. The Hansonburg district: Bingham,
New Mexico. The Mineralogical Record 20, 31–46.


Table 1. Isotopic Ratios of Galena and Cerrusite from the Cerrillos, Magdalena, Hansonburg, and Joyita Hills Mining Districts, New Mexico, U.S.A

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<td>J-1</td>
<td>Joyita Hills</td>
<td>unknown</td>
</tr>
</tbody>
</table>

a sample prepared by dissolution and purified by ion-exchange chromatography
b G= Galena, C= Cerrusite
Figure 1. Map showing the location of ore deposits sampled in this study and regions of glaze ware production discussed in the paper.
Figure 2. Comparison of lead isotopic ratios measured galena from the Mina del Tiro mine in the Cerrillos Hills by single collector-ICP MS, LA-ICP-MS, TIMS, and MC-ICP-MS. ICP-MS, LA-ICP-MS and TIMS measurements are from Habicht-Mauche et al. (2002), and MC-ICP-MS measurements are from this study. Two of the three samples analyzed by MC-ICP-MS are the same as analyzed by Habicht-Mauche et al. (2002). Error bars on TIMS measurements represent errors of 0.1%, and the 2σ external errors on MC-ICP-MS measurements are smaller than the symbols. There is good agreement (within error) among TIMS and MC-ICP-MS measurements made on the same samples. ICP-MS measurements (both dissolution and laser ablation) are far offset from the TIMS and MC-ICP-MS measurements. The error bars shown for ICP-MS measurements do not represent the reported precision, but rather the reported average offset of measured isotopic ratios from their true value in Habicht-Mauche et al. (2002). Error bars for LA-ICP-MS measurements are larger than for ICP-MS, but are not shown.
Figure 3. Lead isotope ratios of galena from the Cerrillos Hills as measured by ICP-MS (Habicht-Mauche et al., 2002) and MC-ICP-MS (this study). All symbols representing MC-ICP-MS measurements are larger than the $2\sigma$ external error. The reported precision of the measurements made by single collector ICP-MS is shown (Habicht-Mauche et al., 2000).
Figure 4. Comparison of lead isotope ratios measured on galena and cerrusite from the Magdalena, Joyita Hills, and Hansonburg mining districts using both ICP-MS (Huntley et al., 2007) and MC-ICP-MS (this study). These mining districts are represented by circles, squares, and triangles, respectively. The ICP-MS measurements shown here represent the same samples that were measured by MC-ICP-MS for this study. Symbols representing MC-ICP-MS measurements are larger than the 2σ external error. External errors for measurements made by single collector ICP-MS are shown (Huntley et al., 2007).
Figure 5. Plot of all lead isotope data collected for this study. All symbols are larger than the 2σ external error.
Figure 6. Comparison of lead isotope ratios measured on lead ores from all sources considered in this study. (Cerrillos Hills – diamonds, Magdalena Mountains – circles, Joyita Hills – squares, Hansonburg – triangles). Colored symbols represent measurements made by MC-ICP-MS (this study) and white symbols represent TIMS measurements taken from Stacey and Hedlund (1983). Black stars represent the isotopic composition of lead ores from other deposits across southwestern New Mexico, as reported by Stacey and Hedlund (1983). Note the similar, but distinct trends formed ores from southwestern New Mexico and ores from the Cerrillos Hills in $^{206}\text{Pb}/^{204}\text{Pb}$ v. $^{207}\text{Pb}/^{204}\text{Pb}$ space. The regression line drawn through ores from southwestern New Mexico is taken from Stacey and Hedlund (1983) and can be interpreted as a secondary isochron with an age of 1.5 Ga. Note that the MC-ICP-MS data for Magdalena, Hansonburg, and the Joyita Hills fall along this trend. A regression line drawn through the data on Cerrillos ores has a distinct slope from that of ores from southwestern New Mexico, and can be interpreted as a 1.7 Ga secondary isochron. All MC-ICP-MS symbols are larger than the 2σ external error associated with the measurements.