

Arizona Salado turquoise: source studies with proton-induced X-ray emission and X-ray diffraction

Arleyn W. Simon, Destiny L. Crider, Tatsuya Murakami, Barry Wilkens

Archaeological Research Institute, School of Human Evolution & Social Change, Arizona State University, Tempe, AZ, USA

Abstract

We compare the composition of turquoise source materials from Arizona to prehistoric blue-green stone artifacts recovered from Salado platform mounds (ca. AD 1275-1450) in the Tonto Basin of Central Arizona. Turquoise samples from known source areas in Arizona including Kingman, Castle Dome, in the Globe-Miami area are compared with others that may have been potential sources of turquoise artifacts recovered from the Salado platform mounds. The complementary techniques of proton-induced X-ray emission (PIXE) for chemical analysis and X-ray diffraction (XRD) for mineralogical signatures are used for non-destructive characterisation of both source area samples and archaeological artifacts. The results of the source area sample characterisations are compared quantitatively with the results of archaeological samples, which are evaluated in terms of their likelihood of being from each of the regional sources. The combination of mineralogical and chemical data to identify source materials provides a more thorough identification of the complex variations within turquoise related materials that may not be distinguished by visual inspection. The PIXE and XRD analysis are compared using a set of multivariate statistics including principal components analysis and discriminant analysis. Additionally, a set of Munsell colour charts specifically for the blue-green range of colours is used to objectively qualify colour in comparison to chemical and mineralogical signatures, as colour alone is not a reliable indicator of composition. The results provide objective data to assess directionality of procurement of turquoise and regional social and economic ties to better understand Salado regional connections during this dynamic period in the American Southwest.

Introduction

The Salado platform mound communities in

the Tonto Basin of central Arizona, USA, and surrounding region were in competition with each other for access to domestic and wild food resources and had differential access to valued objects, such as turquoise, obtained through regional social and trade ties to surrounding areas. During the Gila Phase (AD 1320-1450), the population of the Tonto Basin aggregated into two large Salado platform mound complexes (Rice, 1998; Simon, 1998). In addition to blue-green stones, shell trumpets were recovered from these platform mounds and signify their ceremonial importance.

The Cline Terrace Mound [AZ U:4:33(ASM); Latitude 33.773748 N, Longitude 111.246520 E], located along Tonto Creek at the west end of the basin, was surrounded by a massive boundary wall with an interior earthen berm that served as a catwalk for defensive purposes. Entrance was controlled through gates to the interior plazas and the central elite residences and ceremonial core. An open tower faced the rising sun and the secluded ceremonial plaza. Feasting, including the preparation of agave wine, brought together residents of the surrounding villages. Blue-green stones were recovered from within the ceremonial preparation rooms adjacent to the plaza; residents of this platform mound favoured green colours among these stones (Kim *et al.*, 2003).

At the east end of the Tonto Basin along the Salt River, the population aggregated into the Schoolhouse Point Mound [AZ U:8:24(ASM); Latitude 33.651395 N, Longitude 111.003209 E]. The architecture of this community is more puebloan with elevated rooms, built atop filled cells, clustered around a series of ground-level storage rooms whose roofs form an interior plaza. A boundary wall encloses a large ground-level plaza at the north of the village. Blue-green stones recovered from the site are predominantly blue in colour (Kim *et al.*, 2003).

Materials and Methods

Our primary research questions focus on identifying the social and economic networks by which turquoise and related minerals were obtained. Specifically, did the residents of these two platform mound complexes obtain their blue-green stones from sources within the local region or from more distant locales? Regarding intra-regional relationships, did the two competing platform mound complexes share access to the same sources of blue-green stones, or did they have separate trade networks as is evidenced in obsidian and ceramics (Rice, 1998; Simon, 1998; Simon and Gosser, 2001)?

A previous study using X-ray diffraction (XRD) and proton-induced X-ray emission

Correspondence: Arleyn W. Simon, Archaeological Research Institute, School of Human Evolution & Social Change, Arizona State University, ASU Tempe Campus, 85287-2402 Tempe, AZ, USA. Tel. +1.480.965.6957 - Fax: +1.480.965.7671. E-mail: arleyn.simon@asu.edu

Key words: turquoise, PIXE, XRD, US Southwest, Salado.

Citation: Simon AW, Crider DL, Murakami T, Wilkens B, 2013. Arizona Salado turquoise: source studies with proton-induced X-ray emission and X-ray diffraction. In: RH Tykot (ed.) Proceedings of the 38th International Symposium on Archaeometry – May 10th-14th 2010, Tampa, Florida. Open Journal of Archaeometry 1:e10.

Acknowledgments: this research was carried out with support of the Archaeological Research Institute (<http://archaeology.asu.edu>) using artifacts from the Roosevelt Project Collections; PIXE analysis was conducted at the IBeAM Laboratory (<http://le-csss.asu.edu/ibeam>) of the LeRoy Eyring Center for Solid State Science. Jacob Thorp assisted with PIXE and GUPIX. The XRD analysis was conducted in the Chemistry lab., Arizona State University, Tempe, AZ, USA.

Contributions: the authors contributed equally.

Conflict of interests: the authors declare no potential conflict of interests.

Presented at the 38th International Symposium on Archaeometry – May 10th-14th 2010, Tampa, Florida.

This work is licensed under a Creative Commons Attribution 3.0 License (by-nc 3.0).

©Copyright A.W. Simon *et al.*, 2013
Licensee PAGEPress, Italy
Open Journal of Archaeometry 2013; 1:e10
doi:10.4081/arc.2013.e10

(PIXE) on archaeological samples only (Kim *et al.*, 2003) has shown that there is some differentiation between the artifacts from the two large platform mound communities at the opposite ends of the Tonto Basin. In this study, we add the additional analysis of comparing the composition of turquoise source materials from Arizona to prehistoric blue-green stone artifacts recovered from the two Salado platform mound sites in the Tonto basin of central Arizona (Figure 1).

Samples of turquoise are included from a number of known turquoise source areas (Figure 1) including Kingman (Mineral Peak) 260 km away in Northwest Arizona, Castle Dome and Sleeping Beauty in the Globe-Miami area, located 50-70 km East of the two platform mounds. Other turquoise studies in the area are referenced (Béarat *et al.*, 2003; Welch and Triadan, 1991). A sample from the well known Cerrillos Hills, New Mexico source, located 450

km to the northeast, is included as this was a major extraction site for turquoise for hundreds of years. The complementary techniques of PIXE for chemical analysis and XRD from mineralogical signatures are used to characterize archaeological artifacts (Kim *et al.*, 2003). In this study, PIXE is used to obtain chemical signatures of samples from the potential sources of turquoise artifacts discussed above, and then multivariate statistics are used to compare these to the chemical signatures of the archaeological samples recovered from the two Salado platform mounds. Chemical characterisations of potential source samples were obtained and the archaeological materials evaluated in terms of their likelihood of being from a number of regional sources. The results provide objective data to assess directionality of procurement and social and economic ties to better understand Salado regional connections during this dynamic period of prehistory in the American Southwest.

Archaeological samples

We compare PIXE analysis of 19 cultural turquoise artifacts from the Cline Terrace complex and 22 from the Schoolhouse Point Mound located at opposite ends of the Tonto Basin, Arizona. Both sites were occupied during the Classic period, during the Roosevelt Phase (A.D. 1280-1320) and the Gila phase (A.D. 1320-1450), the latter a time of aggregation into the larger settlements. This study builds upon prior results (Kim *et al.*, 2003) that used XRD and PIXE to determine the variation within the cultural turquoise. It was shown that cultural turquoise includes different minerals, such as antlerite, planerite, azurite, malachite, and quartz. In addition, mixed phases were identified, including quartz and calcite (Figure 2).

For this study, non-turquoise artifacts were excluded except for three artifacts: one antlerite, one planerite, and one with mixed phases of planerite, quartz, and turquoise. Planerite is a member of the turquoise group and is closely associated with mineral turquoise. Antlerite is a sulfate, but is not easily distinguishable from mineral turquoise based on texture and colour. In the previous study (Kim *et al.*, 2003), the colour of each specimen was determined by using blue and green series Munsell colour charts. It was shown that there is no simple correlation between the colour of the specimen and mineralogical composition. Thus, chemical and mineralogical analyses are vital to distinguishing different mineral constituents and sources.

Reference samples

The geological reference samples chosen for this comparative study included samples from Kingman (Mineral Peak) ($n=7$) from north-west Arizona, Castle Dome ($n=4$) and Sleeping Beauty ($n=7$) from the Globe-Miami, AZ area,

and Cerrillos, New Mexico ($n=1$). The Arizona locations are copper mining areas that were known to have been utilised prehistorically; some are still commercial mines. Only the Cerrillos Hills in New Mexico is a now a cultural park. These reference samples were examined using PIXE to obtain chemical signatures for comparison to the cultural turquoise (blue-green stone) artifacts listed above.

Methods

PIXE was chosen to obtain chemical signatures of the turquoise samples because it is a non-destructive method and sensitive in parts per million (ppm) for surface and near surface (0-2 mm) analysis of solids (Feldman and Mayer, 1986; Tesmer *et al.*, 1995). Proton beams were accelerated at both low energy (1.72 MeV) and high energy (2.89 MeV) using

a 1.7 MV Tandemtron accelerator (Cockcroft-Walton type; General Ionex, Newburyport, MA, USA). The proton beam (1 mm²) crosses a 7.8 mm kapton foil window before entering the chamber containing the samples. The chamber was placed under low vacuum ($\gg 100$ mTorr) to avoid air signal and absorption. The Canberra Si(Li) detector (169.8-184.8 eV at 5.9 keV) was placed at a 47° angle from the normal of the sample's surface; the detector has a 2.54 mm Beryllium window with a 1.2 mm gold contact layer. No additional filters were used in front of the detector at low energy (1.72 MeV) to analyse light elements. Turquoise artifacts have large concentrations of copper (Cu) and consequently produce a strong signal causing pile-up. To control this background noise while analysing the heavy elements at high energy (2.89 MeV), foils of Mylar (23 mm) on top of

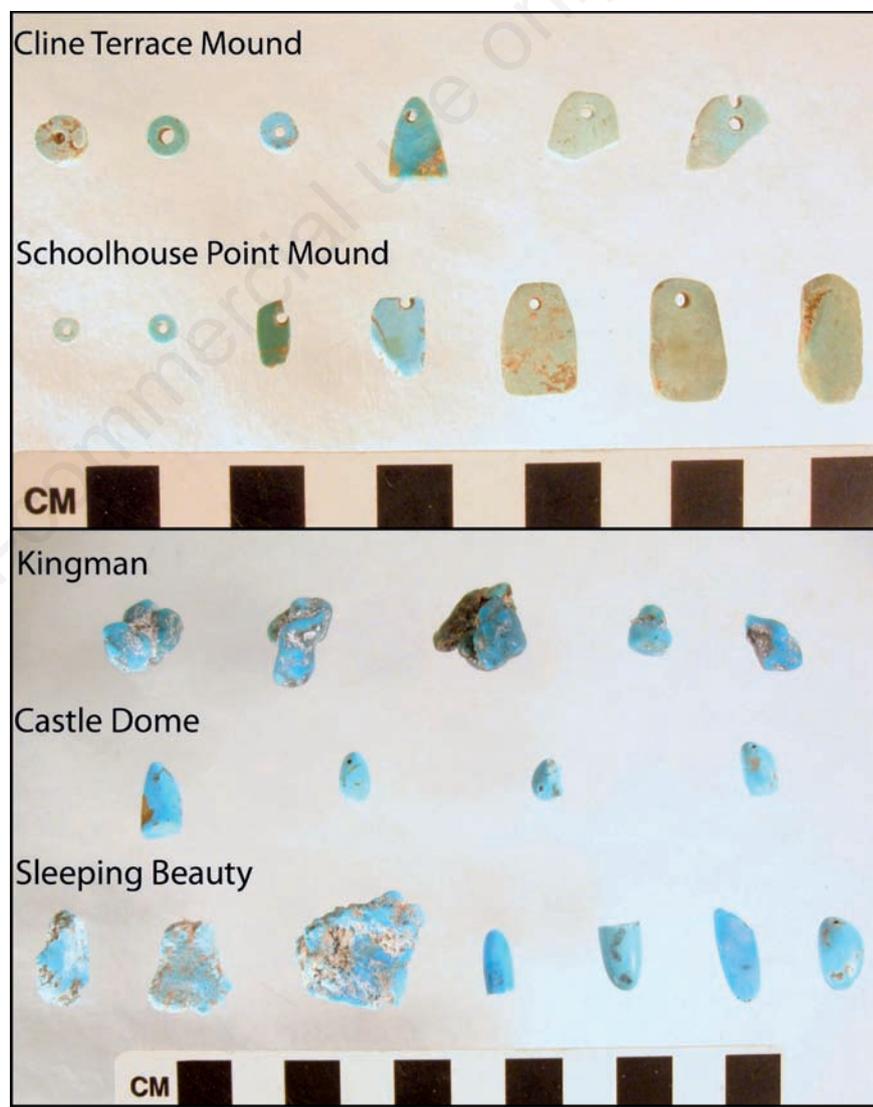


Figure 1. Archaeological blue-green stones (upper set) from the Cline Terrace Mound and Schoolhouse Point Mound in the Tonto Basin, Arizona; Turquoise reference samples (lower set) from Kingman, Castle Dome, and Sleeping Beauty source areas in Arizona.

chromium (16 mm) have been installed in front of the detector, absorbing the peaks of elements lighter than potassium (K) and strongly reducing the iron (Fe) and copper (Cu) signal so that the concentrations of zinc (Zn), arsenic (As), strontium (Sr) and barium (Ba) could be measured in the turquoise artifacts. Two PIXE data acquisitions at two different points were taken for each artifact and up to six data acquisitions were taken for samples showing large chemical variation; the elemental concentrations were then averaged for further statistical analysis. The PIXE detector signals were processed with the GUPIX software package (<http://www.physics.uoguelph.ca/PIXE>). The low-energy spectra were used to obtain the aluminium (Al) to Cu concentrations and the high-energy spectra were used to obtain the heavier elements. The elements used in this analysis include: Al, Si, P, S, K, Fe, and Cu (some elements that were not detected for all the samples were excluded). All the elements were \log^{10} -transformed for subsequent statistical analyses.

Results and Discussion

Preliminary analysis of PIXE chemical compositional data from the turquoise reference samples showed that they are statistically distinct from one another, especially between samples from the Globe-Miami area (Castle Dome and Sleeping Beauty) and the others. Mahalanobis distance-based probabilities of membership (Table 1) successfully assigned each reference sample to its correct source (except for two samples). Based on these positive results, archaeological samples were then compared to reference samples through principal component analysis (PCA), bivariate plots, and Mahalanobis distances.

PCA revealed that over 90% of the variation is explained in the first four principal components (PCs). The first PC is loaded more or less equally on all the elements used in the analysis. The second PC is loaded more on Si, P, and Al than other elements. Examination of the first two PCs (Figure 3) indicates that the archaeological samples overlap the same area as the Globe-Miami sources (Castle Dome/Sleeping Beauty), with the exception of one that is antlerite and is closer to the Cerrillos Hills sample. It is possible that the Cerrillos source contains antlerite. Future research with XRD and additional samples is needed to clarify this.

Examination of bivariate plots also showed the grouping of archaeological samples overlapping with reference samples from the Globe-Miami area, except for the antlerite sample (Figure 4). For both the PCA results and bivariate plots, planerite artifacts (includ-

Table 1. Source assignments based on Mahalanobis distance-based probabilities of membership for archaeological samples from the Tonto Basin, Arizona.

		Castle dome	Sleeping beauty	Kingman	Cerillos hills	Total
Schoolhouse Point	n	9	12	1	0	22
	%	40.91	54.55	4.55	0	100
Cline Terrace Mound	n	6	13	0	0	19
	%	31.58	68.42	0	0	100

Table 2. Mahalanobis distance-based probabilities of membership among reference group samples, showing distinct separation among the sources.

Sample ID	Source	Castle dome	Sleeping beauty	Kingman	Cerillos hills	Best group
T-6	Castle dome	0.5742	0.4173	0.0085	0.0000	Castle dome
T-7	Castle dome	0.6830	0.3139	0.0032	0.0000	Castle dome
T-8	Castle dome	0.9911	0.0088	0.0000	0.0000	Castle dome
T-10	Castle dome	0.5274	0.4695	0.0031	0.0000	Castle dome
T-11	Sleeping beauty	0.3378	0.6349	0.0273	0.0000	Sleeping beauty
T-12	Sleeping beauty	0.0335	0.9308	0.0357	0.0000	Sleeping beauty
T-12	Sleeping beauty	0.0514	0.9411	0.0074	0.0000	Sleeping beauty
T-13	Sleeping beauty	0.6366	0.3604	0.0029	0.0000	Castle dome
T-15	Sleeping beauty	0.2691	0.7215	0.0094	0.0000	Sleeping beauty
T-16	Sleeping beauty	0.0583	0.9402	0.0014	0.0000	Sleeping beauty
T-17	Sleeping beauty	0.4119	0.5686	0.0195	0.0000	Sleeping beauty
T-1	Kingman	0.0011	0.0045	0.9944	0.0000	Kingman
T-2	Kingman	0.0003	0.0312	0.9685	0.0000	Kingman
T-3	Kingman	0.0002	0.0004	0.9994	0.0000	Kingman
T-3	Kingman	0.0000	0.0000	1.0000	0.0000	Kingman
T-4	Kingman	0.1741	0.1600	0.6659	0.0000	Kingman
T-5	Kingman	0.1755	0.7236	0.1008	0.0000	Sleeping beauty
T-5	Kingman	0.0029	0.0724	0.9247	0.0000	Kingman
T-9	Cerillos hills	0.0000	0.0000	0.0000	1.0000	Cerrillos hills

ID, identification code.

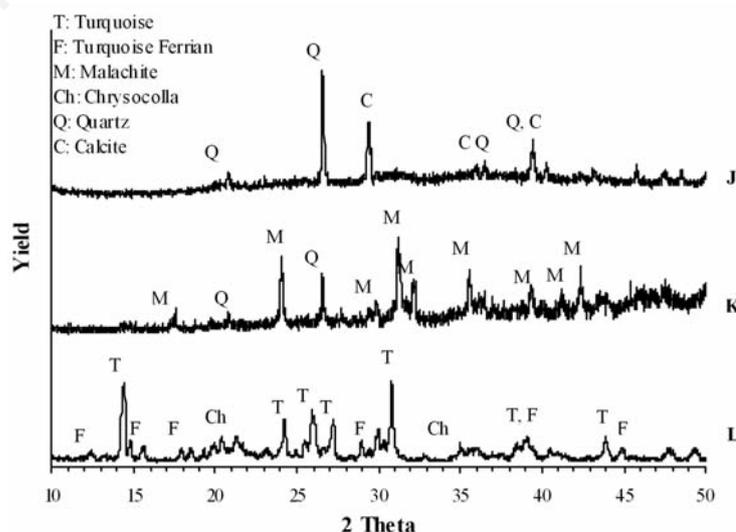


Figure 2. Example of X-ray diffraction analysis of archaeological samples: X-ray diffractogram of mineral combinations showing complex peak patterns: J) quartz and calcite (CaCO_3) from Cline Terrace Mound (RPMS 32952); K) malachite and quartz from Schoolhouse Point Mound (RPMS 15640); L) turquoise, ferrian turquoise [$\text{Cu}(\text{Al},\text{Fe})(\text{PO})(\text{OH})\cdot 4\text{H}_2\text{O}$] and chrysocolla [$(\text{Cu},\text{Al})_2\text{H}_2\text{SiO}_5(\text{OH})_4\cdot n\text{H}_2\text{O}$] from Schoolhouse Point Mound (RPMS 17274). (Adapted from Kim et al., 2003; ©IOP Publishing. Reproduced with permission: all rights reserved).

ing the one with mixed phases) are closely associated with turquoise ones. This raises the possibility that the Globe-Miami sources contain planerite. On-going XRD analysis of reference samples will clarify this point.

Mahalanobis distance-based probabilities of

membership (Table 2) indicate that most archaeological samples can be assigned to the Globe-Miami sources (Castle Dome/Sleeping Beauty). Although there are other turquoise sources in the nearby area that were not yet included in this study, it is likely that both

Schoolhouse Point Mound and Cline Terrace Mound obtained most of their blue-green stones from the same and/or nearby local sources. One of the Schoolhouse Point Mound samples was assigned to Kingman, but some of Kingman samples are chemically similar to those of the Globe-Miami area as seen in the PCA plot (Figure 3). Further research with XRD is necessary to determine the differences between these two distant sources. In this study, no samples were assigned to the Cerillos Hill reference which is at a great distance from the study area.

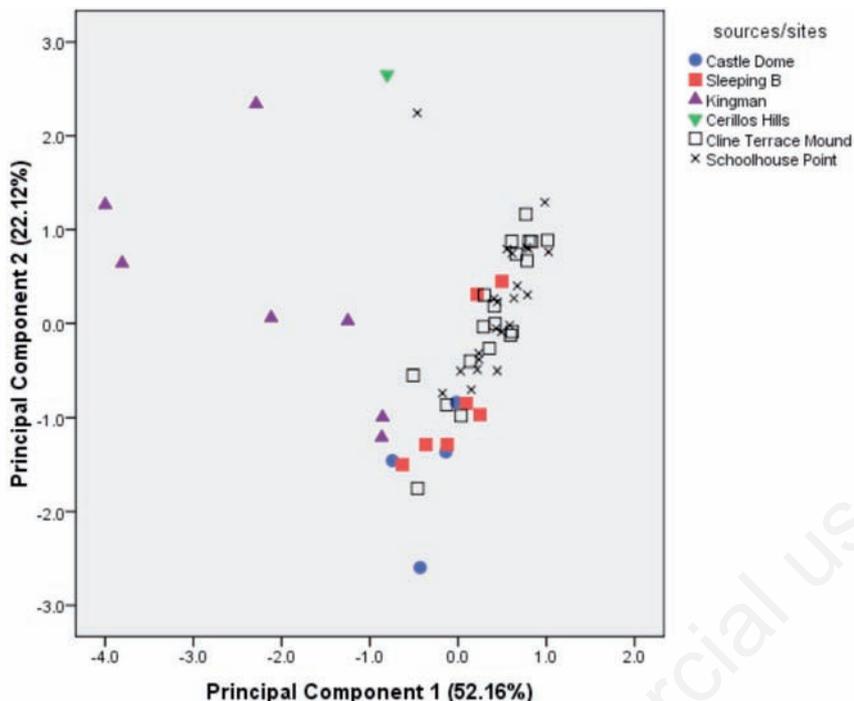


Figure 3. Plot of first two principal components of the dataset comparing the relationship of archaeological samples and turquoise source samples. Most archaeological samples are closely plotted to the Castle Dome and Sleeping Beauty reference samples, the ones closest geographically to the sites.

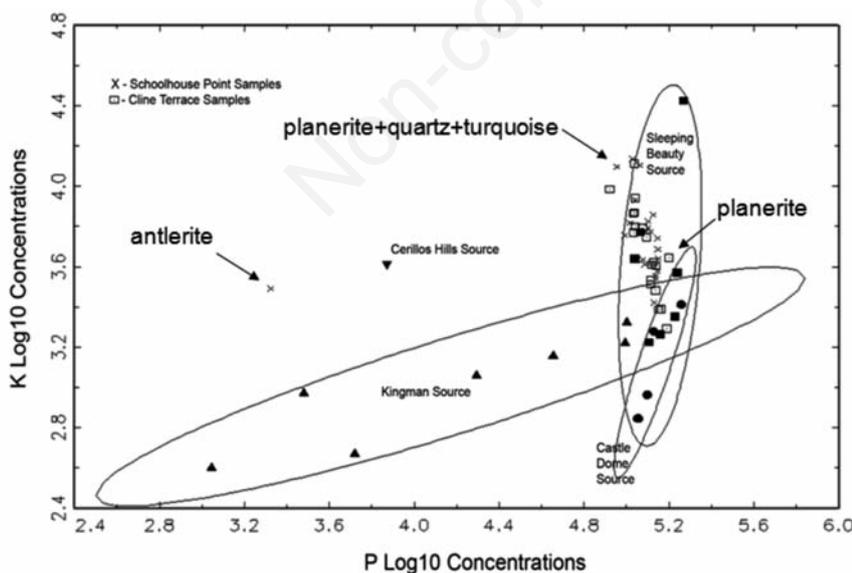


Figure 4. Plot of elemental concentrations (Log_{10}) for potassium (K) and phosphorus (P) showing the distribution of archaeological blue-green artifacts from Cline Terrace Mound and Schoolhouse Point Mound compared to those of source reference samples, especially local sources represented by Castle Dome and Sleeping Beauty in the Globe-Miami, Arizona area, just East of the Tonto Basin.

Conclusions

This preliminary study shows that: i) different turquoise sources can be chemically distinguished through PIXE analysis; ii) some sources might contain minerals other than turquoise, which points to the importance of XRD analysis for provenance study to understand mineralogical differences within the turquoise group; and iii) the residents of Schoolhouse Point Mound and Cline Terrace Mound complexes had access to the same and/or nearby local sources, in similar proportions. The preference of green hues at the west end (Cline Terrace) and blue hues at the east end (Schoolhouse Point) of the Tonto Basin is still culturally meaningful, even though the chemical and mineralogical signatures may cross-cut these visual qualities of the stone artifacts.

This relatively equal access to turquoise related stones from the Globe-Miami area contrasts with the exchange patterns of some decorated ceramics and obsidian, both categories of which derive from farther distances. Both ceramics and obsidian analyses identified different regional social and economic spheres for the two platform mounds (Simon and Gosser, 2001), with Cline Terrace favouring ties to the northwest, while the Schoolhouse Point Mound favoured ties to the east. The blue-green stones or cultural turquoise were highly valued and ideologically charged objects and might have been circulated through different networks than ceramics and obsidian. This indicates multiple spheres of social interactions, through which different kinds of materials were exchanged within and beyond the study region.

References

- Béarat HA, Simon AW, Murakami T, 2003. Chemical and mineralogical characterization of some turquoise samples from the US 60 Florence Junction Project.

- Archaeological Research Institute, School of Human Evolution & Social Change, Arizona State University ed., Tempe, AZ, USA.
- Feldman LC, Mayer JW, 1986. Fundamentals of surface and thin-film analysis. North-Holland Publ., Amsterdam, The Netherlands.
- Kim J, Simon AW, Ripoche V, Mayer JW, Wilkens B, 2003. Proton-induced x-ray emission analysis of turquoise artefacts from Salado Platform Mound Sites in the Tonto Basin of central Arizona. *Meas Sci Technol* 14:1579-89. In: J.W. Mayer and M. Menu (eds.), Special feature: archaeometry. IOP Publishing Ltd., Bristol, UK.
- Rice GE, 1998. A synthesis of Tonto basin prehistory: the Roosevelt archaeology studies, 1989-1998. Department of Anthropology, Arizona State University ed., Tempe, AZ, USA.
- Simon AW, 1998. Salado ceramics and social organization: prehistoric interactions in Tonto basin: the Roosevelt archaeology studies 1989-1998. Department of Anthropology, Arizona State University ed., Tempe, AZ, USA.
- Simon AW, Gosser DC, 2001. Conflict and exchange among the Salado of Tonto basin: warfare motivation or alleviation? In: GE Rice, S LeBlanc (eds.), *Deadly landscapes: case studies on prehistoric Southwest warfare*. University of Utah Press, Salt Lake City, UT, USA, pp 219-238.
- Tesmer JR, Nastasi M, Barbour JC, Maggiore CJ, Mayer JW, 1995. *Handbook of modern ion beam materials analysis*. Materials Research Society ed., Pittsburgh, PA, USA.
- Welch JR, Triadan D, 1991. The Canyon Creek turquoise mine, Arizona. *Kiva* 56:145-64.

Non-commercial use only