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## STUDY

Pottery vessels from the Chilean Diaguita Culture show alteration of the **black** paint that was used for its decoration. Loss of cohesion, change in color from an intense **black**, to a **reddish brown/greenish brown** layer, and modification in composition account for this alteration.

## WHERE

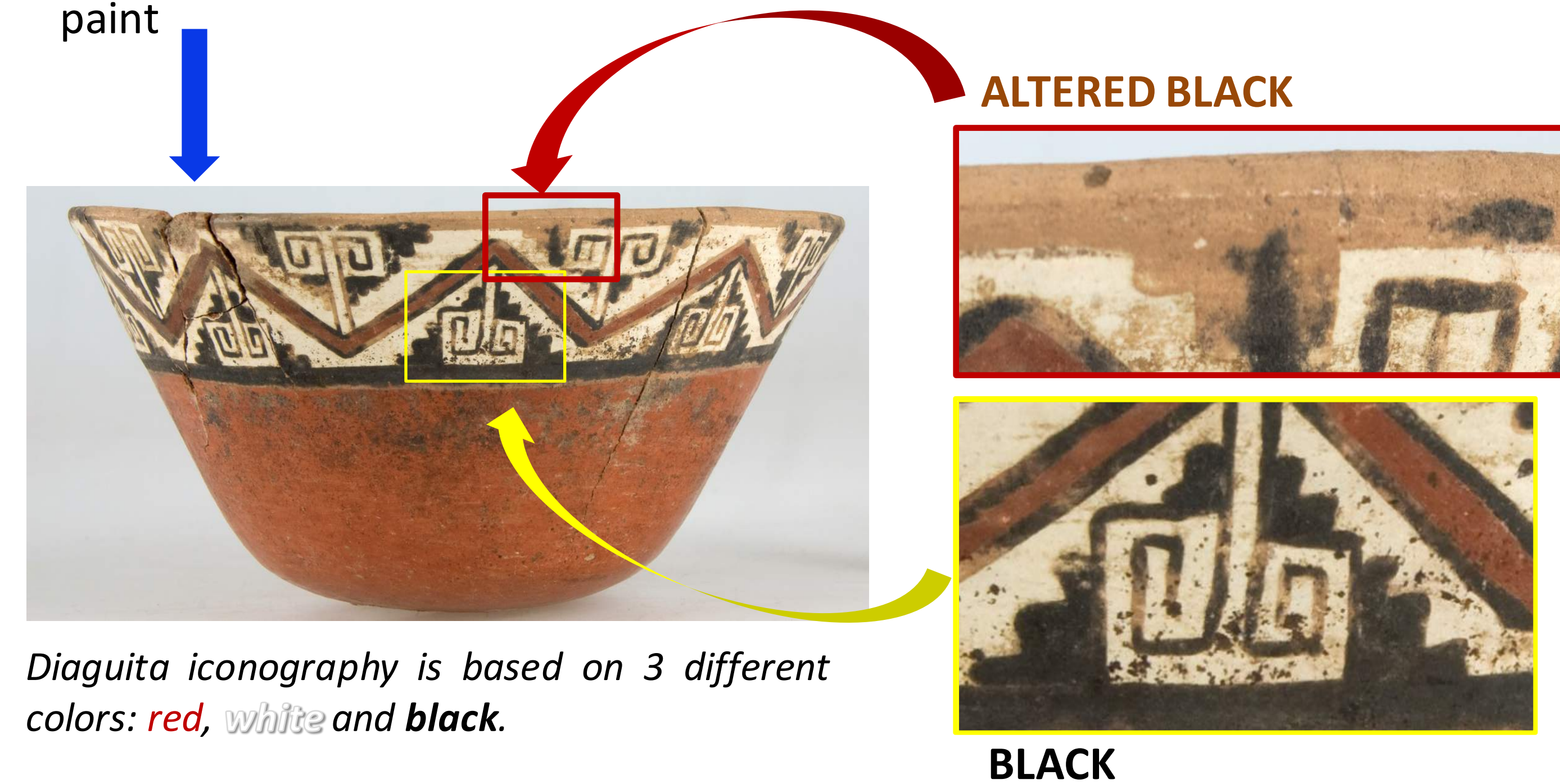


The Diaguita Culture occupied N-central Chile and NW Argentina (900-1536A.D.). In Chile they inhabited 5 valleys: Copiapó, Huasco, Choapa, Elquí and Limarí

## WHAT WE WORKED WITH

- Raw pigment from archaeological sites of El Olivar (**white** and **red**) and Ovalle (**green**)

- Potteries with iconography that present the **black** and **altered black** paint



Diaguita iconography is based on 3 different colors: **red**, **white** and **black**.

## ANALYSIS

Espectrocolorimetry

X-ray fluorescence and EDS: C, O, Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, Mn, Fe, Ni, Cu, Ba

X-ray diffraction: paint and raw pigment

Cross section: paint differentiation and firing process



atacamite,  $\text{Cu}_2\text{Cl}(\text{OH})_3$   
antlerite,  $\text{Cu}_3(\text{SO}_4)(\text{OH})_4$   
quartz,  $\text{SiO}_2$   
alunite,  $\text{K}(\text{Al}_3(\text{SO}_4)_2(\text{OH})_6)$

Bowl, Diaguita Phase I. La Serena Archaeological Museum



## THE GREEN ISSUE

**Cu** minerals are the major components for this **green** pigment. **BUT** green is **NOT** part of the Diaguita iconography. **HOWEVER** one pottery showed a rare partial **green** paint in combination with **black** on its surface. Surprisingly, mineral associations of the **green** paint and the raw pigment are basically the same.

## THE BLACK ISSUE

**Cu** is the major component of the **black** paint mainly as **tenorite** ( $\text{CuO}$ ) and with lesser Fe, as hematite ( $\text{Fe}_2\text{O}_3$ ). **Tenorite** may be the primary source of **black** for the Diaguita iconography. **BUT tenorite** has not yet been found as pigment in archaeological sites. In Andean prehistoric cultures C, Mn and Fe minerals are the primary sources of **black**, **NOT tenorite**. 2 origins are proposed for its presence: **NATURAL** or **MANUFACTURED**

### NATURAL

It occurs in oxidized zone of primary copper sulfide deposits. Chile is the world leader in Copper production. It has a long pre-hispanic mining tradition. Copper deposits containing **tenorite** are present in the Diaguita territory.

### CONSIDERATIONS

- Making pigments is linked to metallurgy (1). The Diaguita metalwork is well represented with a preference for **Cu** and **Cu** alloy ornamental objects and tools. It is assumed to be of local origin (2)
- Exchange of goods could also provide primary material
- Tenorite** can form in certain alkaline conditions over other **Cu** compounds (3)



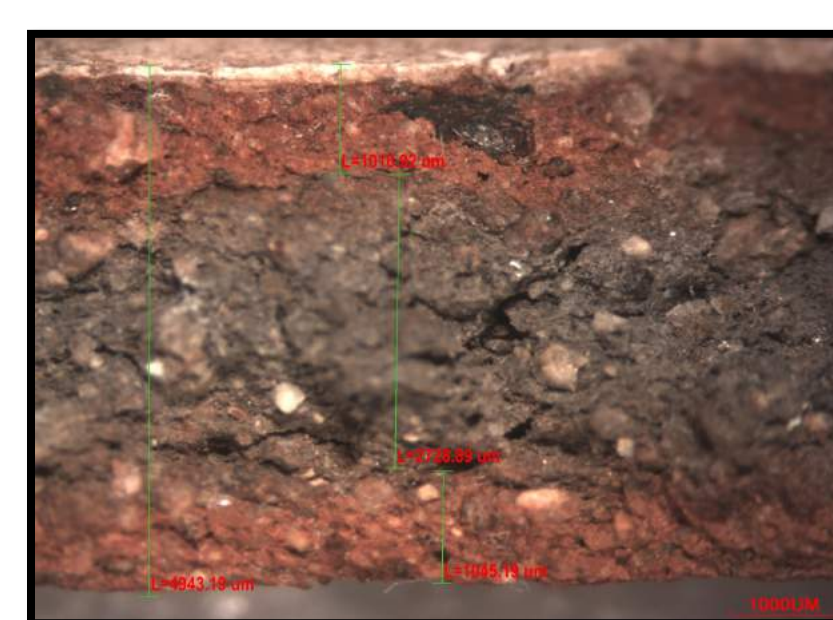
Modern Cu deposits in Diaguita territory. Archaeological sites are in yellow dots.

### MANUFACTURED

Most **Cu** minerals can transform to **tenorite** when heated in air, like **malachite**, **azurite** (4) **atacamite**, **antlerite**, **cuprite**, **chalcocite**. Temperature varies. These minerals occur within the study area.

### CONSIDERATIONS

- Tenorite** pigment could be prepared first, then used as a **black** paint **OR** transformed during heating
- Atacamite** could provide material for the formation of the **black tenorite** via firing process. What would be the necessary quantity of pigment for coloring?
- Firing process is important. Some Andean cultures did not heat the **black** and **red** paint on their potteries. Numerous Diaguita potteries show an incomplete oxidation process during firing



Incomplete oxidation during firing. Zoomorphological bowl. Diaguita Phase II. Limarí Museum

## SOME THINGS TO THINK ABOUT

- The use of **tenorite** as **black** pigment could differentiate Diaguita from their neighbors.
- Could the Diaguita have ingeniously heated **atacamite** or **cuprite**, and end up with **black tenorite**?
- Study of paste and coloring layers in microscope (SEM) will give more information on firing and alteration processes

## THE ALTERED BLACK ISSUE

Physical and chemical mechanisms are responsible for the alteration of the **black** paint. "Transformation" from **black** to **brown** corresponds to an impoverishment in **Cu** compared to Fe. **Hematite** ( $\text{Fe}_2\text{O}_3$ ), quartz ( $\text{SiO}_2$ ) and **cuprite** ( $\text{Cu}_2\text{O}$ ) are present.

Cross sections from sherds from Limarí Museum show multiple scenarios of alteration



**Black** layer with **brown** interface  
Bowl, Diaguita, phase II



**Rare green** lens between **black** and **brown** layers. **Black** sample from this sherd showed **ajoite**,  $(\text{K}, \text{Na})_3\text{Cu}_{20}\text{Al}_3\text{Si}_{29}\text{O}_{76}(\text{OH})_{16} \cdot 8(\text{H}_2\text{O})$   
Zoomorphical bowl, Diaguita, phase II



**Brown** layer with small lens of **black**  
Bowl, Diaguita, phase II



**Brown** layer over **white**  
Bowl, Diaguita, phase II

### CONSIDERATIONS

Key parameters for understanding the alteration processes are:

- Manufacture
- Firing processes and techniques
- Soil dynamics and composition
- Alteration during burial and/or post excavation?

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