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Review

The presence of calcite in archeological ceramics

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Abstract

The present work describes the methods for detecting and classifying calcite in archeological ceramics, the forms of calcite and their interpretation in archeometric terms. Calcite appears in form of coarse granules and fine particles, and its origin can be primary or secondary. Coarse granules can be polycrystalline or mono-crystals of calcite. Fragments of shells, fossils or microfossils are also found. Primary calcite is the initial calcite preserved in low-fired pottery. Secondary calcite, formed after the ceramic firing, may be reformed (re-carbonated) calcite, precipitated calcite or calcite from alteration. The firing can cause the formation of a ‘reaction rim’ around coarse granules of calcite, while strong decomposition of coarse calcite causes the formation of ‘calcite ghosts’. The identification of the forms of calcite gives information on raw materials, the firing temperature and the manufacturing technology of the pottery.

Keywords: Archeological ceramics; Primary calcite; Secondary calcite; Laboratory analyses

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1. Introduction

Calcite is frequently found when investigating ancient ceramic materials, typically pottery, from archeological excavations. Its utilization in the ceramic can be related to different technological reasons.[1] The calcite may derive from the raw material but also be incorporated by precipitation or alteration during burial of the ceramic shards.[2,3] Therefore, it is important to know which type of calcite is present, because this information can often be transformed into conclusions of archeological interest. The reasons for the presence of calcite can be investigated by the archeometric methods[4] that will be hence appropriately illustrated. Finally the connection between archeometric results and presence of calcite will be also explained.

Two main types of ceramics were manufactured in ancient times: calcareous (calcite-rich) ceramics and siliceous (non-calcareous) ceramics. In the calcareous ceramics, fine particles or crystals of calcite are dispersed in the fired ceramic paste. Such ceramics were manufactured from carbonatic clay raw materials, which were used in order to obtain sintering at lower firing temperatures. Calcareous ceramics are found along the archeological periods: the Neolithic,[5] the Chalcolithic,[6] the Bronze Age,[7,8] the Iron Age,[9] the Hellenistic,[10] the Roman.[11]

In ancient pottery, calcite is frequently found also as coarse grains or fragments incorporated in the ceramic paste. Coarse granules in the ceramics are known as temper, non-plastic component, and inclusions. The ancient potters frequently used fragments of limestone and chalk composed of polycrystalline calcite for tempering the raw material during production of vessels.[9,12] Fragments of mono-crystal calcite were commonly added for tempering of cooking vessels.[13]

The presence of calcite affects the ceramic firing. Above the de-carbonation temperature, the calcite decomposes, carbon dioxide gas (CO_2) is released, and free-lime (CaO) is formed. Under prolonged ceramic firing the de-carbonation takes place at temperatures between 600 and 800 °C, depending on the form of the calcite, the impact of the clay and the firing conditions.[14,15] The calcite resists longer in: coarse granules, well crystalline form, very fast heating rates, short soaking time in the critical temperature interval, and in conditions of reducing atmosphere inside the pottery kiln during the firing.[16]

After the ceramic firing, a reformed (re-carbonated) calcite (re-carbonated calcite) is crystallized from the free-lime.[17] Thus, the source of the reformed calcite is the thermal decomposition of the initial calcite contained in the raw material. The hygroscopic free-lime picks up moisture from the air, forming calcium hydroxide [$Ca(OH)_2$]. Then, the latter slowly reacts with atmospheric carbon dioxide (CO_2) and reformed calcite is crystallized.

In ceramic firing above 800 °C, the free-lime from the de-carbonated calcite generates new Ca-silicates by reaction with the fired clay. These newly formed silicates include minerals such as gehlenite, anorthite, larnite and diopside-wollastonite.[18–20] The formation of these phases reduces the amount of the free-lime, and consequently the possibility of re-carbonation.

Then, an alteration process of gehlenite in the ceramics may bring to the formation of a hydrated aluminate–silicate of calcium, called wairakite, together with calcium hydroxide, which is transformed into calcite.[21]

2. Methods for detecting and classifying calcite

2.1. Polarizing optical microscopy

The calcite is detected and classified through the petrographic method, by examination of a thin section of the ceramics under a polarizing optical microscope in two conditions: parallel (PPL) and cross (XPL) polarization.

The examination of the ceramics at the polarizing optical microscope likely is the best method for distinguishing the different forms of calcite. But the preparation of thin sections is a destructive technique; consequently it is used when it is possible to destroy a quite large piece of ceramics. This technique enables the identification of coarse and fine particles and the evaluation of their amount and grain size distribution.

The spathic, micritic or organogen nature of the calcite can be identified, and the presence of rounded or angular edges and reaction boundaries as well. Finally, this method permits the identification of ‘calcite ghosts’, i.e. voids left to the place of calcite granules, as well as ‘reaction rims’, i.e. edges of reaction formed around calcite granules.

2.2. X-ray diffraction (XRD)

The calcite is identified by examination of a powder of the ceramics with XRD diffractometer. This technique gives the mineral composition of the crystalline phases, but it is not sensitive to the pseudo-amorphous phases of the fired clay. The minerals are identified by their characteristic peaks observed in the diffractogram.

Since the calcite is observed in powder obtained by grinding a ceramic fragment, this technique is especially useful when there are not coarse granules of calcite. The diffractogram of samples containing primary calcite generally does not show