He+ Irradiation of Quartz for the Identification of Ceramic Forgeries Aged by Radiation

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INTRODUCTION

Thermoluminescence (TL) is a powerful tool for authenticating ceramic artifacts, with an accuracy of ±20-30% that is generally sufficient for differentiation between genuine objects and fakes [1]. However, one of the biggest problems about the great diffusion of TL as dating tool is that counterfeiters have learned in time various tricks to mislead the authentication. Whereas the assembling of old and new parts or the carving from ancient but worthless artefacts can be quite easily discovered by means of other techniques, the "aging" of an object induced by artificial irradiation with X or γ rays cannot be detected with certainty so far [2].

The chosen approach for overcoming this issue is the observation of the effect of α particles irradiation on the quartz grains contained in the clay matrix. This kind of irradiation is only present in naturally irradiated samples, and almost impossible to reproduce. An α particle is a Helium nucleus (He^{2+}) with a significant mass, higher than for β or γ particles and hence capable of inducing lattice damage. Since the penetration range of an α particle is smaller than those of β or γ ones, only the surface shell of quartz crystals is involved with the interaction and could show the characteristic traces. In geology, the effect of α particles on quartz is well known as the consequence of constant irradiation, for millions of years, of the portion of crystal surrounding radioactive inclusions, in particular Uranium and Thorium. The visible effect results in the formation of a luminescent halo, easily detectable with cathodoluminescence (CL) imaging [3].

EXPERIMENTAL

The granulometric selection of coarse quartz grains was performed using a 40 μm mesh sieve on the ceramic powder collected from five different archaeological bricks. Only one sample (B1) provided an acceptable yield (set at 25% w/w >40 μm minimum) for further treatment of the material: a brick from the base of Paung Gu Temple in Bagan (Myanmar), dated back to the II-late IV century AD. A treatment for 1 hour with HCl 10% w/w followed by 1 hour in CH_3COOH 10% w/w allows the elimination of, respectively, carbonates and organic impurities.

The common use of HF for the dissolution of feldspars, however, is unsuitable in this case since this acid erodes also the external shell of the quartz grain, that is exactly the area of interest for this study. After removing traces of fillosilicates with washing in acetone, partial enrichment in quartz was achieved with magnetic separation on the >315 μm fraction, using a Frantz L-1 magnetic separator at the Geosciences Department of the University of Padova. Further selection was then performed via handpicking of the grains under microscope. Finally, the grains were embedded in epoxy resin, polished to expose the core and carbon coated (Figure 1).

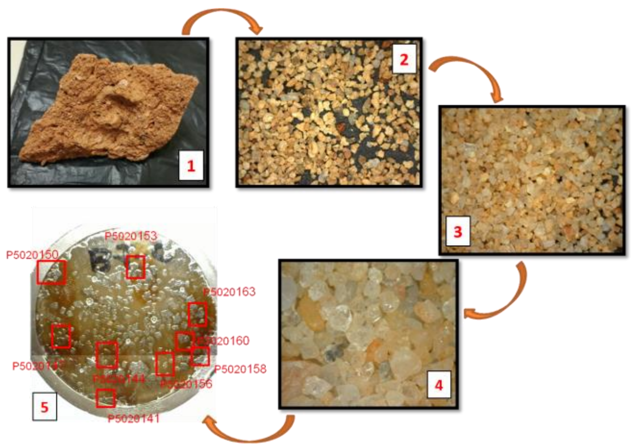

Fig.1 Quartz separation procedure: the analyzed Paung Gu Temple coarse brick (1). Grains after sieving and chemical treatment (2), magnetic separation (3) and handpicking (4). Embedded and polished grains (5): areas analyzed with cold-CL are highlighted.

In order to obtain a visual and immediate reference of the effect of α particles on natural quartz, the embedded grains were irradiated with a microbeam of He+ accelerated ions at the AN2000 accelerator. The size of the beam was about 6 μm and an energy of 1.8 MeV for the ions was selected, aiming at best simulating the natural particles. However, it must also be taken into account that α particles lose the greatest part of their energy at the end of their path inside the material and the highest concentration of generated defects will be at the maximum penetration range (R). From SRIM [4] simulations, a 1.8 MeV α particle in quartz (density = 2.65 g/cm^3) can reach a R value of 5.22 μm, hence a second value of energy (0.6 MeV, R = 1.99 μm) was also employed, corresponding to a R compatible with the area of the crystal investigated with a CL probe (15 keV electrons, R about 2 μm). Three different values for fluences (10^{15}, 10^{16} and 10^{17} ions/cm^2) were tested as well on three 100x100 μm^2 adjacent areas of the same crystal.

The cold-CL apparatus is the one described in [5], equipped with a new Peltier-cooled Olympus DP74 camera for image acquisition. An accelerating voltage and current of 15 kV and 500 μA respectively were used during the measurements.

RESULTS AND DISCUSSION

The CL images acquired after irradiation at the Earth Science Department of the University of Torino clearly show the squared shape of the targeted areas, with increasing CL intensities as the fluence increase (Figure 2). Also, as expected, the effect is more visible for the lower energy value: for 0.6 MeV He^+ ions with a 10^{17} ions/cm^2 fluence the irradiation outcome results in a completely different CL color, turning from green to blue. The CL variation visible between the inner and outer part of the squared area is due to the gaussian shape of the beam.

The possible natural effect of α particles on the external shell is not distinguishable with this resolution, hence further observations will be necessary for a definitive comparison. It will also be useful to perform additional damaging session via α irradiation at different energies and fluences, possibly with a subsequent observation of the grain in cross section.

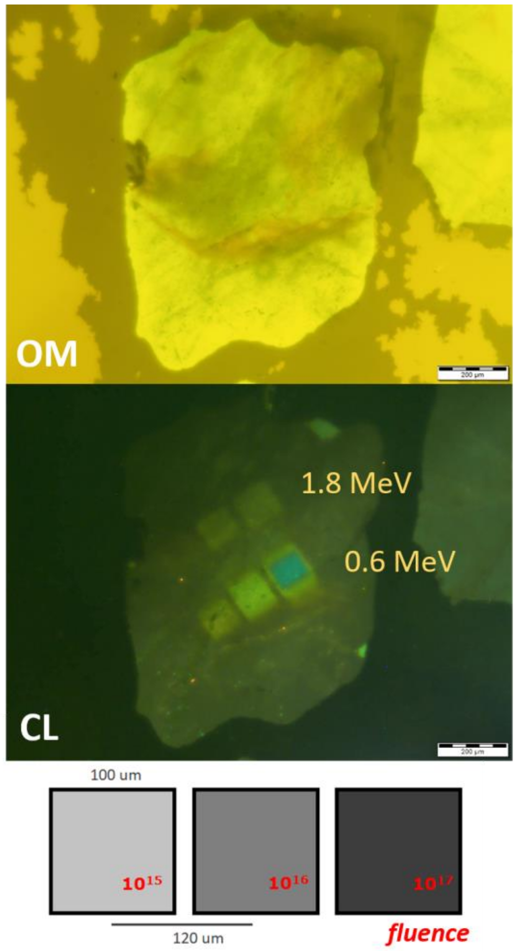

Fig.2 Optical Microscope (above) and cold-CL (below) images of the same quartz crystal from Paung Gu Temple coarse brick; He^+ irradiation was performed in six different areas, with 1.8 MeV (upper row) and 0.6 MeV (lower row) energy combined with three fluence values (10^{15}, 10^{16} and 10^{17} ions/cm^2). Scale bars are 200 μm long. A scheme of the irradiation pattern is also reported.

CONCLUSIONS

The He^+ irradiation of natural quartz induces cathodoluminescence emission phenomena that can be compared to the effect of natural α irradiation. The preliminary results obtained have to be extended to a wider set of samples, exploiting various energies and fluences to create a reference database. This can be a good starting point for a new protocol that aims at identifying fake ancient ceramics aged via artificial irradiation.

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