IONOLUMINESCENCE AND CATHODOLUMINESCENCE IN MARBLES OF HISTORIC AND ARCHITECTURAL INTEREST*

M. CORAZZA,¹ G. PRATESI,² C. CIPRIANI,² A. LO GIUDICE,³ P. ROSSI,⁴ E. VITTONE,³ C. MANFREDOTTI,³ E. PECCHIONI,¹ C. MANGANELLI DEL FÀ⁵ and F. FRATINI⁵

¹Dipartimento di Scienze della Terra, Università di Firenze, via G. La Pira 4, 50121 Firenze, Italy ²Museo di Storia Naturale, Sezione di Mineralogia e Litologia, Università di Firenze, via G. La Pira 4, 50121 Firenze, Italy

³Dipartimento di Fisica, Università di Torino, INFM Unità di Torino Università, via Giuria 1, 10125 Torino, Italy

⁴Dipartimento di Fisica, Università di Padova, via Marzolo 8, 35131 Padova, Italy

Ion beam induced luminescence (IBIL) was applied, along with cathodoluminescence (CL), on seven samples of marbles of historic and architectural interest. The CL colours, observed in a cold cathode device, have been related to the IBIL spectra. Moreover, a detailed analysis of the IBIL spectral features has made it possible to disclose the influence of the chemical composition and to emphasize the crystal-chemical role of the Mn²⁺. Beyond the chemical information and the crystal-chemical interpretation, the spectra are recognized as being valuable in the field of archaeological studies for their significance as fingerprints of marbles, giving information on their nature and origin.

KEYWORDS: ION BEAM INDUCED LUMINESCENCE, MARBLE, Mn²⁺ ION, CALCITE, DOLOMITE, PROVENANCE

INTRODUCTION

The chemical, mineralogical-petrographical and physical characterization of marbles is undoubtedly important for knowledge of their geological history and for the study of their genetic environment. Furthermore, since marbles have been often used, in several civilizations, as a raw material for buildings and sculptures, a detailed investigation is also interesting in order to discover the provenance as well as the trading path. In recent years, many efforts have been made to identify effective methods for the discrimination of marbles (Craig and Craig 1972; Manfra et al. 1975; Lazzarini et al.1980; Calia et al. 1992); for example, cathodoluminescence microscopy (Fairchild 1983; Barbin et al. 1989, 1992a,b; Ramseyer et al. 1989, 1992), electron paramagnetic resonance spectroscopy (Baietto et al. 1999; Attanasio et al. 2000) and quantitative fabric analysis (Schmid et al. 1999).

In particular, the study of luminescence has been proven to be very suitable to obtain information on the nature and origin of marbles.

In fact, it is widely known that luminescence in natural calcite and dolomite is mostly due to transition elements, and in particular to Mn^{2+} ions, and corresponds—as suggested by Walker *et al.* (1989)—to the electron transition in the outer, partially filled 3d shell (namely, the electronic transition from the excited state ${}^4T_{1g}$ to the ground state ${}^6A_{1g}$). The crystal field

⁵CNR—Centro Studi sulle Cause di Deperimento e Metodi di Conservazione delle Opere d'Arte, via Alfani, 74, 50121 Firenze, Italy

^{*} Received 5 January 2001; accepted 11 June 2001.

C University of Oxford, 2001