INTRODUCTION

Glassmaking has been an industrial activity for more than four thousand years. Flat glass, however, has been only extensively produced and used for architectural purposes for the last one thousand years, following the building of cathedrals and religious buildings in Central Europe in the early Middle Ages. Thus, the remnants of medieval stained glass windows constitute a part of our cultural heritage that has been exposed to environmental damage over centuries. This provides an exceptional opportunity to test glass durability and to understand long-term environmental corrosion processes on glass.

In addition, in historic buildings, both the rock and the glass have been exposed to the same atmospheric conditions, which allows for comparison of the mechanisms of decay on both materials. The main purpose of this paper is to provide new insights into the biodegradation processes of stained glass and associated mineralization. To do so, several European Mediterranean case studies have been chosen and studied, taking into account the fact that the decay of historic glass seems to appear at an earlier stage when compared with most Central European glasses.

State of the art

Glass is made up of several components: network formers, network modifiers (flux and stabilizers), and coloring elements (Fernandez Navarro 1985; Newton and Davison 1989; Römich 1999). The main network former of medieval stained glass is silica. Its content determines the physical and chemical behavior and the stability of silicate glasses. Flux decreases the temperature at which the mixture (essentially the silica) melts and is made up of alkaline elements (Newton and Davison 1989; Römich 1999). In medieval times, a flux was introduced into the mixture as vegetal ash. Stabilizers (lime, magnesia, etc.) make the glass strong and more water resistant. Phosphorus is a common component of medieval glasses (Pérez-y-Jorba et al. 1984); it can also act as a network-former (Römich 1999) and can be attributed to the ashes used as raw material to obtain alkali, especially potash (Freestone 1993). Furthermore, several metals (Cu, Co, Mn, etc.) were used to provide color to the glass (Bamford 1977; Newton and Davison 1989). If we consider the main elements in the glassy mesostase, historic glass can be classified, from a chemical point of view, into several types (Newton and Fuchs 1988; Brill 1999, and references therein). Most European medieval stained glass produced between the 12th and 15th century can be considered potassic in composition. Recent research on coeval European Mediterranean glass shows the continuation of a Roman-like sodium glassmaking tradition. Despite this, there is a mixture of pieces of glass of both compositions (usually restricted to different colors) in the same Mediterranean stained-glass windows (Julia et al. 2001; Garcia-Vallès and Vendrell 2002; Gimeno and Pugès 2002 in Spain; Gimeno, unpublished data, for Siena Cathedral, Italy).