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Cathodoluminescence and electron probe micro-analysis of silcretes and puddingstones: towards a better understanding of silcretization and sourcing quartzitic materials

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ABSTRACT

We have investigated quartz cement in silcretes and puddingstones from uppermost Paleocene to lowermost Eocene, terrestrial to coastal and shallow marine sediments in north France and Belgium using cathodoluminescence (CL) and trace element electron probe micro-analysis (EPMA). The syntaxial cement overgrowing quartz grains exhibits mostly dark to dark-blue and yellow-brown CL In Ti-rich silcretes. The fine-grained cement that is found capping flint pebbles and as illuviated material in intergranular porosity has a typical milky-white to yellow CL. EPMA analyses of Ti, Fe, Al and K indicate that substituting Al and K are enriched in dark-blue CL quartz with most measured Al concentrations ranging from 1000 to 5000 ppm. Detrital grains and syntaxial quartz with yellow-brown CL typically have $<$100 ppm Al. We interpret the Al-rich syntaxial cement as indicative of silicification under acidic conditions. Sub-aerial exposition of sediments containing both acid-liberating (pyrite) and Al-rich (feldspar and clays) minerals would provide a favourable, but not exclusive mechanism for the formation of silcretes. Our analyses furthermore suggest that silicification occurred under the influence of a fluctuating water table, with restricted chemical mobility during low water table episodes. In Ti-rich silcretes, up to 8% Ti is concentrated along with subordinate Fe and Al in a heterogeneous, microcrystalline cement, which typically forms illuviated structures. This Ti-rich cement predates syntaxial quartz overgrowth and indicates vadose processes as well. The CL and trace-element characteristics of silcretes are potential fingerprints, which could be used for provenance analysis.

1. Introduction

Terrestrial deposits such as silcretes are important for reconstructing the evolution of the Earth's subsurface where marine series are lacking. Understanding silicification processes in silcrete is crucial in deciphering their environmental significance, especially when they are associated with intervals of climate change such as the PETM (Paleocene-Eocene Thermal Maximum). Despite the typology of silcrete and its associated environment have gained much progress (e.g. Summerfield, 1983; Thiry, 1999; Nash and Ullyott, 2007), many aspects of silcrete formation still remain obscure (source of silica, precipitation mechanisms, associated environment, timing of silicification, etc.). Although we will not discuss in detail silcrete classification, silcrete typology is here derived from Thiry (1999), with the usual distinction between quartzitic ("groundwater") and Ti-rich ("pedogenetic") silcretes.

Cathodoluminescence (CL) and trace-element geochemistry of quartz cement are increasingly used for investigating the diagenetic evolution of sandstones (Demars et al., 1996; Kraishan et al., 2000; Boggs and Krinsley, 2006; Götte et al., 2013). However, these techniques have not previously been much applied to sedimentary rocks that have undergone supergene silicification such as silcrete. CL permits a very detailed picture of the growth history of quartz to be obtained, but few conclusive interpretations have been published so far. This is in part due to our poor understanding of CL activation in quartz (Götze, 2009). From a technical point of view, measuring trace-element concentration in thin quartz cements is still challenging as it requires high sensitivity together with high spatial resolution. Electron Probe Micro-Analysis EPMA has sub-micron analytical capability and can detect trace-elements at a concentration down to a few tens or hundreds of ppm depending on the element.

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In this study, we document the CL characteristics in relation to the Al, K, Ti and Fe trace-element composition of quartz cements in a selection of silcretes and puddingstones samples from Northern France and Belgium. These elements were chosen because they are commonly present in quartz in sufficient concentration to be measured with the EPMA. The results obtained so far show that the combined CL/EPMA approach can advance our understanding of the formation processes of silcrete and of the origin of the cement.

2. Materials and methods

2.1. Brief description of the samples

Silcrete samples from 12 localities in Northern France and Belgium (Paris Basin) were collected for this study (Fig. 1). All 12 originate from supergene silicification that affected uppermost Paleocene to lowermost Eocene ("Sparnacian") terrestrial and coastal detrital sediments (Quesnel et al., 2009; Dupuis, 1979). Many silcretes are relict features within residual formations that resist weathering because of their chemical durability. In addition, silcrete-bearing formations are commonly truncated, hence the detailed original sedimentary context of silcrete is often difficult if not impossible to investigate. More stratigraphical and sedimentological information on silcretes in the studied area is provided in Dupuis (1979) and Quesnel (1997).

When observable, the macromorphology of the silcrete in the field varies from metric to decametric, irregularly silicified masses developed in arenaceous sediments, most frequently with a typical elliptical, flat shape and a mamillated surface. At Grandglise, the silcrete occurs in a 10 m thick section with silicification being more intense upward.

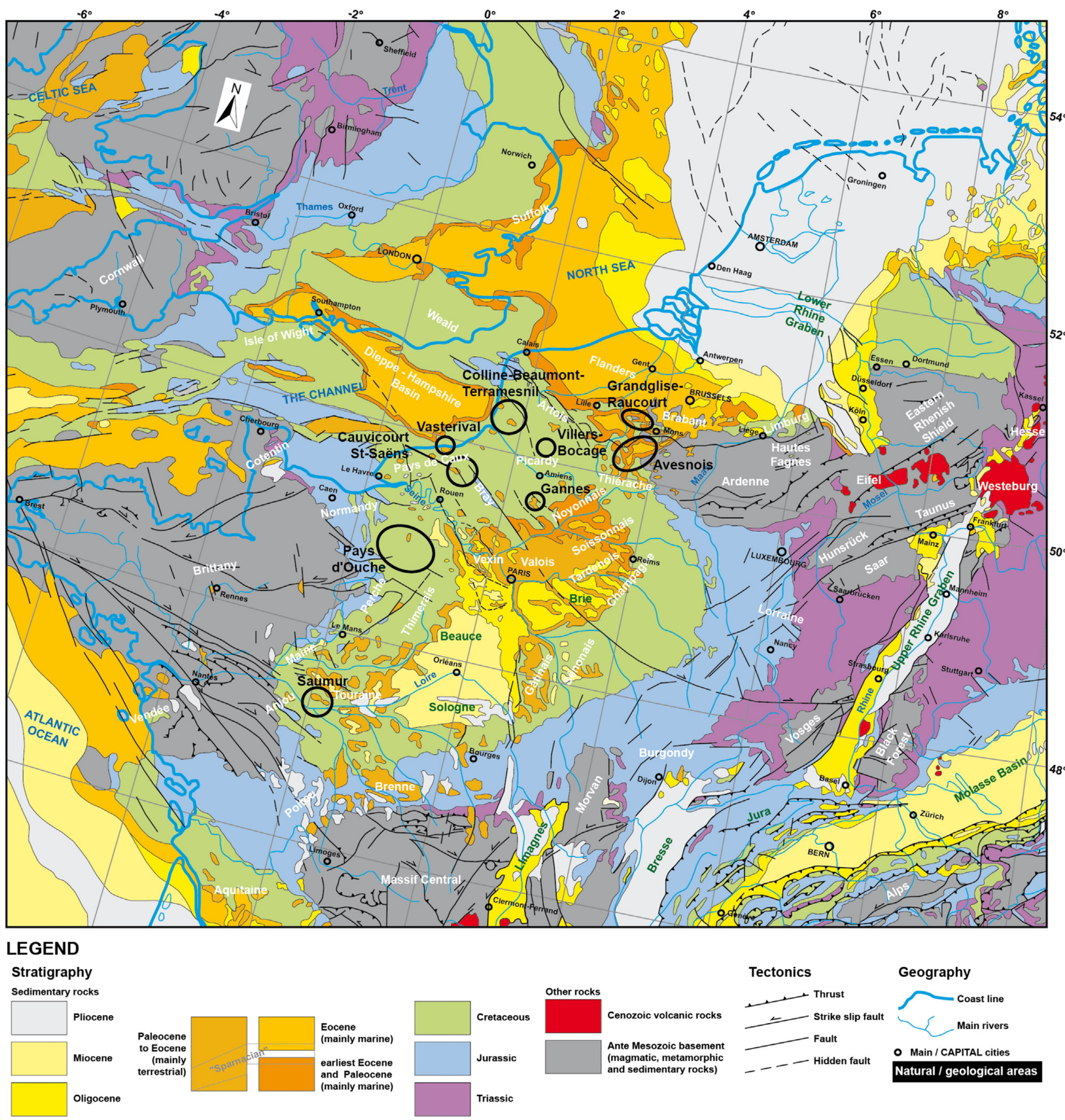

Fig. 1. Location map of the studied samples (European geological background modified after Iakovleva et al., 2013 and IGME, 2005).