Quaternary Geochronology 12 (2012) 65–73

Contents lists available at SciVerse ScienceDirect

Quaternary Geochronology

journal homepage: www.elsevier.com/locate/quageo

Research paper

Quantification and spatial distribution of dose rate relevant elements in silex used for luminescence dating

Christoph Schmidt [a,*], Thomas Pettke [b], Frank Preusser [c], Daniel Rufer [b], Haino Uwe Kasper [d], Alexandra Hilgers [a]

[a] Institute for Geography, University of Cologne, Otto-Fischer-Str. 4, 50674 Köln, Germany
[b] Institute of Geological Sciences, University of Bern, Baltzerstrasse 1+3, 3012 Bern, Switzerland
[c] Department of Physical Geography and Quaternary Geology, Stockholm University, 10691 Stockholm, Sweden
[d] Institute for Geology and Mineralogy, University of Cologne, Zülpicher Str. 49a, 50674 Köln, Germany

ARTICLE INFO

Article history:
Received 20 January 2012
Received in revised form
15 May 2012
Accepted 20 May 2012
Available online 29 May 2012

Keywords:
Silex
Flint
Thermoluminescence, TL
Microdosimetry
ICP-MS
LA-ICP-MS

ABSTRACT

Thermoluminescence (TL) is routinely used to date heated lithic artefacts which mostly consist of silex (a mixture of amorphous opal and microcrystalline chalcedony). Analytical investigations of bulk samples confirmed that these materials contain considerable concentrations of radioactive elements, generating an internal dose rate contribution. Common dosimetric models assume the latter to be homogeneous throughout the sample. If this assumption would prove invalid, this will result in systematic errors in the calculated age, especially in the course of so called 'hot spots' of α-emitters (and associated local changes in α-sensitivity) and the dose response characteristics of α-radiation. Laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) analyses of 22 silex samples are presented here, quantifying element concentrations at several tens analytical spots per sample. Along with radioactive elements (K, Rb, U, Th), another 21 major, minor and trace elements were measured in order to allow characterization of the impurities present in most of the samples. The dataset provides a detailed picture of the spatial distribution of radionuclides and hence of the uniformity of the internal α- and β-dose rate. It is shown that the silex itself mostly contains low amounts of K (<0.1 wt.%), U (<1.0 μg g^{-1}) and Th (<0.4 μg g^{-1}), and dosimetrically negligible Rb concentrations. Systematically higher concentrations are obtained by ICP-MS measurements of the bulk samples. This matches with the finding that impurities (veins, inclusions) often yield significantly elevated radionuclide concentrations, up to two orders of magnitude higher than the silex values. These veins and inclusions, for example Ca or Mg carbonates and Fe–Mn-oxy-hydroxides, lead to steep gradients mainly in the internal α-radiation field. Alternative approaches are required to account for the non-uniform internal dose rate and improve the reliability of TL dates of problematic samples.

1. Introduction

When exposed to ionizing radiation, certain minerals are capable of storing part of the absorbed energy; they act as radiation dosimeters. Events to be dated are related to the erasure of the accumulated radiation dose (reset of the clock), for example by heat which is accompanied by emission of light (thermoluminescence, TL). Accordingly, the amount of measured luminescence in the laboratory is a measure of the time elapsed since the last resetting event. Ionizing radiation is generated by naturally occurring radionuclides (those of the elements K, U and Th and their decay products and, to a lesser degree, Rb) in the surrounding of the dosimeter and/or within the dosimeter itself. The rate of energy transfer (dose rate) determines the speed of luminescence signal (dose) increase over time. As a consequence, correct dose rate determination is crucial to obtain valid age information, since the age is calculated by dividing dose by dose rate. Especially in the case of self-dosing (internal dose rate) of minerals, the distribution pattern of radionuclides can have considerable impact on the effective dose rate, due to micro-scale interaction effects of ionizing radiation and the mineral.

Analogous to quartz, SiO_2 in amorphous, micro- and crypto-crystalline form can also be used as radiation dosimeter. These materials, generally termed 'silex', were used by ancient humans to produce tools, and frequently these tools were heated by fire, either intentional or by accident. In case the heating temperature reached

* Corresponding author. Tel.: +49 0 221 470 8830; fax: +49 0 221 470 5124.
E-mail address: c.schmidt@uni-koeln.de (C. Schmidt).

1871-1014/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
doi:10.1016/j.quageo.2012.05.006

about 400–450 °C, the geological luminescence signal was reset and the newly accumulated signal can be used to estimate the time elapsed since ancient heating.

While there are established methods for dose determination by TL (e.g. Valladas and Gillot, 1978; Aitken, 1985; Mercier, 1991; Valladas, 1992; Richter and Krbetschek, 2006), only simple models are applied for internal dose rate assessment, i.e. uniform distribution of radionuclides is usually assumed in the age calculations (Mercier et al., 2007; Richter et al., 2007). Several studies approached the question whether this assumption is justified or not, but the spatial resolution of the methods so far employed was too limited to allow for conclusive statements or the investigation was based on one element only (Aspinall and Feather, 1972; Malik et al., 1973; Selo et al., 2009). However, the presence of non-uniform and/or locally high concentrations of radionuclides ('hot spots') entails microdosimetric effects and consequently systematic errors in the age. Tribolo et al. (2006) studied and calculated such effects in detail for their samples from Blombos Cave (South Africa) and obtained differences in age of up to 25%, depending on the type of U distribution in the samples (uniform or clustered). Therefore, knowledge about the spatial uniformity in internal radiation is crucial to avoid microdosimetric effects on the resulting age.

In contrast to quartz, silex samples often contain considerable amounts of radionuclides, as shown by bulk measurements using for instance neutron activation analysis (Valladas, 1985; Mercier et al., 1995). This difference is reflected by the optical appearance; whereas quartz is mostly white or transparent, silex appears in a variety of different colors and textural compositions. However, most silex samples contain not just pure silica (SiO_2) but also inclusions trapped during formation and mineral phases which entered later into the considered material.

A previous study investigated the distribution of α- and β-emitters in 21 different silex samples, detected by autoradiography (Schmidt et al., in press). It is shown that radionuclides are mainly unevenly distributed and occur more or less clustered. Moreover, comparison of the radiation patterns with visual appearance suggests that the presence of radioisotopes is to some extent bound to minerals other than SiO_2.

In this study the qualitative approach of Schmidt et al. (in press) is expanded by laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) measurements on the same samples to obtain spatially resolved, quantitative information on the concentration of all relevant radioactive elements, down to ng g^{-1} concentration levels. Spatially resolved radionuclide concentrations are then opposed to ICP-MS measurements of the bulk samples for assessing the dosimetric influence of impurities. Furthermore, along with K, Rb, U and Th 21 major, minor and trace elements were measured by LA-ICP-MS for geochemical characterization of the non-siliceous phases and inclusions in the specimens.

2. Materials and methods

The samples investigated in this study are the same as described in Schmidt et al. (in press), except for one additional sample (T1). For covering both a wide range of different materials and provenances 22 samples were chosen from Central and Eastern Europe (Germany, Belgium, Poland, Austria, Italy, Hungary and Romania), Jordan and Morocco (Table 1).

With respect to the discussion below it is important to consider the common procedures and protocols applied in silex dating. Sample preparation for TL measurements usually includes crushing of the solid rock into small fragments or powder and the obtained sample material is then treated like a granular sample during the subsequent measurement procedures. Whereas single aliquot regenerative dose (SAR) procedures are established in optically stimulated luminescence (OSL) dating of sediments (e.g. Murray and Wintle, 2000), TL dating of heated material is widely based on multiple aliquot additive and/or regenerative dose techniques (e.g. Aitken, 1985; Mercier et al., 1995; Valladas et al., 2007). The latter often suffers from non-efficient normalization to account for aliquot-to-aliquot differences in luminescence properties.

LA-ICP-MS allows for sequential analysis of major, minor and trace elements from a given spot in solids with a spatial resolution of a few tens of μm. The system used here comprises a Geolas 193 nm ArF excimer laser system (Lambda Physik) combined with an Elan DRC-e quadrupole ICP-MS (Perkin Elmer). Optimization strategies and operating conditions were similar to those reported in Pettke (2008). Ablation rates were tuned to ca. 0.2 μm per pulse and laser pulse rate was set to 10 Hz. Laser beam sizes were generally 120 μm, except for better resolution of hot spots or zonations as indicated by autoradiography. Here, beam sizes as small as 44 μm were employed. This translates to 80 μm deep ablation craters for 40 s signal duration. Data reduction was done with the SILLS program (version 1.1.0, Guillong et al., 2008) by carefully evaluating every transient signal with special attention to the radioactive elements K, Rb, U and Th, including spike filtering. Signal sections of homogeneous element intensities were selected for integration. SRM 610 from NIST was used as an external standard material and element abundances were calculated by summing up major element oxides to 99.5 wt.% (e.g. Halter et al., 2002). A total of 24 elements were quantified at typical precisions

Table 1
List of investigated samples. The geological origin of some specimens is still unidentified.

Internal code	Denomination	Provenance	Geological origin
A1R	Chalcedony	Ain Zora, Morocco	Tertiary
A2R	Chalcedony	Ain Zora, Morocco	Tertiary
M1R	Tabular hornstone	Abensberg-Arnhofen, Franconia, Germany	Upper Jurassic
M4R	Flint	Orsbach, Northrhine-Westphalia, Germany	Upper Cretaceous
M5R	Flint	Lousberg, Northrhine-Westphalia, Germany	Upper Cretaceous
M9RII	Flint	Rullen, Belgium	Upper Cretaceous
M11R	Quartzite	Lenderscheid, Hessia, Germany	Tertiary
M12R	Flint	Holy Cross Mountains, Poland	Jurassic
M13R	Chalcedony	Salzkammergut, Austria	Unknown
M15R	Flint	Rijckholt, St. Geertruid, Belgium	Upper Cretaceous
M16R	Trigonodus hornstone	Dinkelberg, Baden-Württemberg, Germany	Middle Triassic
M17R	Banded hornstone	Kleinkems, Baden-Württemberg, Germany	Upper Jurassic
M20R	Flint	Caredo, Lessinian Mountains, Italy	Unknown
M26R	Flint	Fehmarn, Baltic Sea, Germany	Cretaceous
N1	Flint	Petra region, southern Jordan	Cretaceous
O2R	Radiolarite	Szentgál, Bakony Mountains, Balaton, Hungary	Middle Jurassic
O4	Jasper or chalcedony	Coşava, Banat, Romania	Unknown
O5	Cornelian	Coşava, Banat, Romania	Unknown
O6	Cornelian	Coşava, Banat, Romania	Unknown
O7	Cornelian	Coşava, Banat, Romania	Unknown
O8	Chalcedony	Românești, Banat, Romania	Unknown
T1	Flint	Baltic Sea	Cretaceous