Chemical Geology 294-295 (2012) 190–202

Contents lists available at SciVerse ScienceDirect

Chemical Geology

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

Research paper

Chemical element imaging for speleothem geochemistry: Application to a uranium-bearing corallite with aragonite diagenesis to opal (Eastern Siberia, Russia)

Guillaume Devès [a], Anne-Sophie Perroux [b], Thomas Bacquart [a], Cyril Plaisir [a], Jérôme Rose [c], Stéphane Jaillet [d], Bassam Ghaleb [e], Richard Ortega [a], Richard Maire [b,*]

[a] Centre d'Etudes Nucléaires de Bordeaux Gradignan, CENBG, CNRS UMR 5797, Université Bordeaux 1, BP120 Le Haut Vigneau, 33175 Gradignan, ANR Climanthrope, France
[b] CNRS UMR 5185 ADES, Université Bordeaux 3, Maisons des Suds, 12 Esplanade des Antilles, 33607 Pessac, programme ANR Climanthrope, France
[c] CEREGE UMR 6635 CNRS, Aix-Marseille Université, Fédération ECCOREV, Equipe SE3D, Europôle de l'Arbois, BP 80, 13545 Aix en Provence Cedex 4, France
[d] CNRS UMR 5204 EDYTEM, Université de Savoie, Campus scientifique, 73376 Le Bourget-du-Lac, France
[e] Laboratoire GEOTOP, Université du Québec à Montréal, P.B. 8888 succ. centre-ville, H3C 3P8, Montréal, QC, Canada

ARTICLE INFO

Article history:
Received 28 January 2010
Received in revised form 18 May 2011
Accepted 7 December 2011
Available online 14 December 2011

Editor: D.B. Dingwell

Keywords:
Chemical imaging
Speleothem
Uranium
Diagenesis
Opal
Siberia

ABSTRACT

Two complementary image-based microanalysis methods, digital autoradiography of radioactive elements and X-ray fluorescence microspectroscopy (micro-XRF), were used to study the geochemistry of a speleothem from Eastern Siberia. Our objective was to show the interest of these micro-chemical methods to investigate the distribution of U and some other elements as Ca, Sr, and Si in speleothems. The sample studied was a corallite concretion that formed slowly by the precipitation of minerals from moisture that had condensed underground. Polished sections of the sample revealed alternating laminas of gray calcite and white aragonite. The concretion, which is older than 400 Kyr (U/Th-TIMS), showed no signs of detrital contamination ($^{230}Th/^{232}Th > 10{,}000$). Digital autoradiography and XRF analyses indicated exceptionally high uranium contents, ranging from 3–10 to more than 1300 $\mu g \cdot g^{-1}$ in different areas of the sample. Element maps for calcium (Ca), uranium (U), strontium (Sr) and silicon (Si) showed inverse correlations between Ca and U and between Ca and Si, but there is a strong correlation between Si and U. Under the optical microscope, the low Ca appears as corrosion voids, which were found to contain uranium-enriched amorphous silica replacing areas of aragonite and, in some cases, calcite. This postgenetic amorphous and uraniferous silica is composed of two kinds of opal: opal A formed by large microspheres of 30–40 μm in diameter and a gray opal CT with irregular lepispheres. This late opal, dated around 385–412 Kyr, is probably due to a special volcanic event formed by uraniferous glass ashes easily soluble by meteoric waters, as suggested by the presence of volcanic suite in the fine fraction of the opal. Opal precipitated after speleothem crystallization by evaporation or cryogenic supersaturation. The study of this exceptional concretion shows the value of direct chemical imaging methods, as they easily revealed the presence and distribution of U in the concretion, and allowed an unusual case of opal diagenesis in a carbonate speleothem to be described. Given the value of speleothems as geo-chronometers and recorders of environmental changes at different time scales, from season to isotopic stage, this methodology opens new perspectives in understanding the geochemical system and consequently the validity of radiometric datings, U/Th and U/Pb, especially in speleothem samples.

1. Introduction

The present study aims to show the methodological interest of geochemical imaging methods to describe speleothems, especially those who have suffered diagenetic phenomena. These methods have been applied to a complex example of uranium-rich and partially diagenised speleothem from Baikal area in Siberia (Russia). The application of these direct analytical techniques to the analysis of natural samples can give specific information about how sediments are formed (Ortega et al., 2003, 2005; Böning et al., 2007). Chemical imaging provides information about the spatial distribution of elements in that sample. Although it is yet to be widely applied to underground deposits, chemical element imaging may allow uncovering new information that other techniques cannot reveal, providing hence an excellent complement to traditional multi-parameter analysis tools (Ellwood et al., 2004; Riera et al., 2004; Perroux, 2005; Quinif et al., 2006).

This study combined two analytical methods that have rarely been applied to endokarst deposits: digital autoradiography and micro-X-ray fluorescence spectroscopy (micro-XRF). Combining these two chemical imaging techniques, both of which give spatial resolution

* Corresponding author. Tel.: +33 5 56 84 68 34; fax: +33 5 56 84 68 55.
E-mail address: rmaire@ades.cnrs.fr (R. Maire).

0009-2541/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.chemgeo.2011.12.003

at micrometric scale (10–100 μm for micro-XRF and 50 μm for autoradiography), opens new perspectives for improving our understanding of the parameters which control the geochemical system: elemental composition and diagenesis; that is to say how some parameters can affect the formation and the postgenetic evolution of speleothems, thereby increasing the quantity and accuracy of the paleoenvironmental information that can be extracted from underground archives or on the contrary modifying some chemical characteristics. Although Baikal region is one of the most studied natural regions in the world, it is always full of enigmas for ecosystems (Timoshkin, 1999) as well as for paleoenvironment (Tanaka et al., 2007). This specific example of speleothem shows all the potential of endokarstic proxys as speleothems.

2. Geological context and sample description

The studied region is the Tazheran massif that lies in Eastern Siberia on the arid west bank of Lake Baikal, (Fig. 1). This massif is formed by Upper Archean and Lower Proterozoic marbles and calciphyres of the Olkon series, a very complex melange of marbles and magmatic mingling (Khrenov, 1983; Fedorovsky et al., 1993). More than 100 caves, 13 of which are over 500 m long, have been found (Pulina and Trzcinski, 1996; Trofimova, 1996, 2005, 2007). Some of them as Aya Cave have been dated as mid-Miocene based on the remains of rodents, lagomorphs, tortoises and snakes. The analyzed corallite speleothem was collected from Mechta Cave, 823 m long and 52 m deep, which is considered as a tertiary cave with old red argilites, but without fauna and pollens (Filippov, 1989, 2004). Ice formations and carbonated concretions as stalagmites, and recent flow deposits were also found in the cave. In polished section, the collected sample showed dense and homogenous laminated crystallization of calcite and aragonite. Under visible light microscope, irregular layers, corresponding to dissolution voids, were also found, especially in the aragonite laminas. These voids had colorless or light-gray infillings looking like typical amorphous silica of opal.

3. Imaging analysis methods and TIMS dating

The geochemical analysis and imaging methods used in the present study have two major advantages: 1) they provide precise and complete information about sample inorganic chemical composition, and 2) they present this composition as a two-dimensional map that gives an immediate picture of the relationships between the different elements. Such chemical maps are extremely useful for studies of natural samples, which can have very heterogeneous compositions. In speleothem studies, maps reveal the presence and location of contaminants allowing direct observation of speleothems internal structures, which are highly sensitive to site effects. These methods are also non-destructive and do not require much sample preparation. The general principle of digital autoradiography and X-ray fluorescence

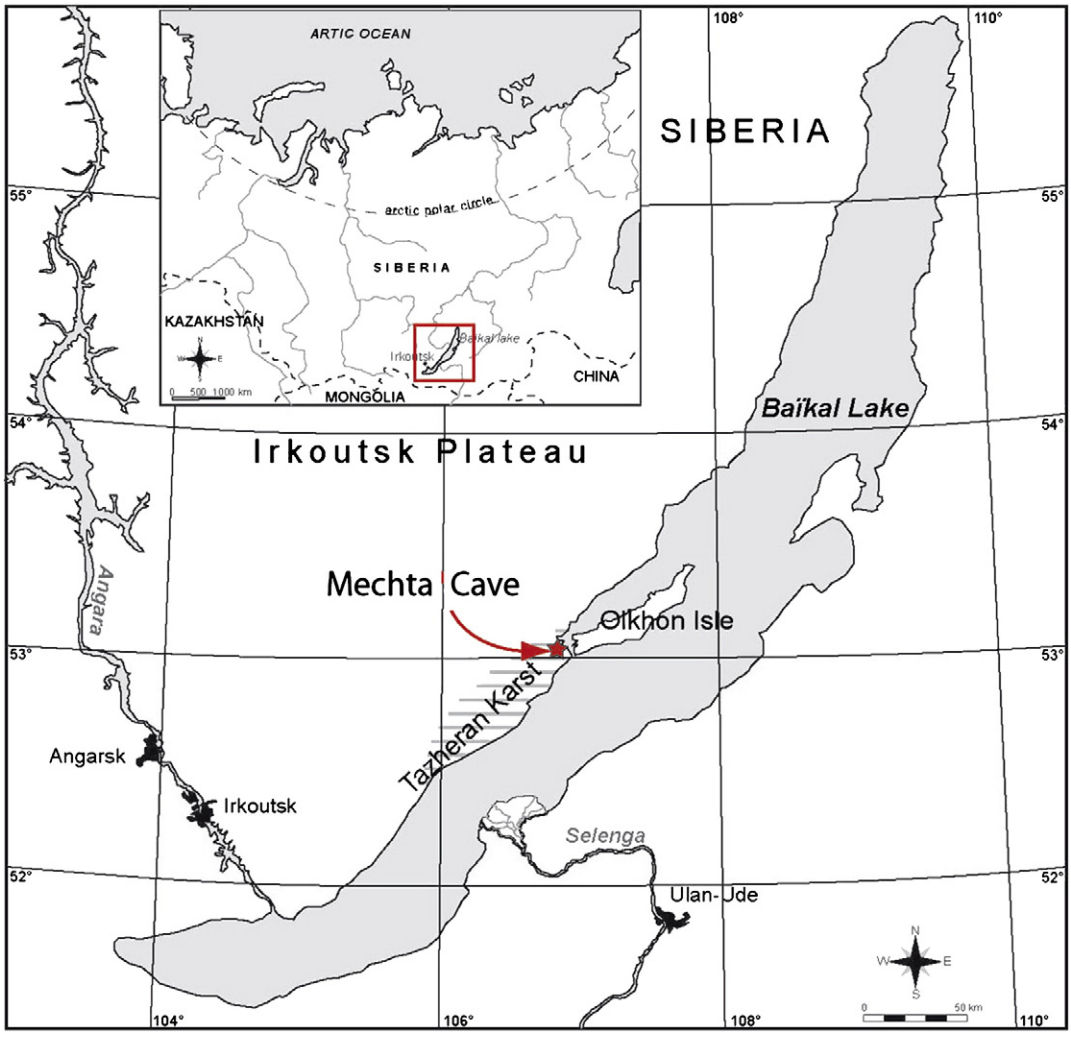

Fig. 1. Location map of the Tazheran massif (Priolkhon plateau) and Mechta Cave (Baikal). The studied area is located on the western coast of Baikal Lake in the Upper Archean marbles.