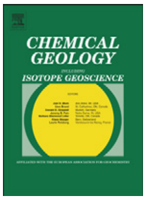
Chemical Geology 357 (2013) 18–28

Contents lists available at ScienceDirect

Chemical Geology

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



Hydrothermal and unexpected diagenetic alteration in Permian shales of the Lodève epigenetic U-deposit of southern France, traced by K–Ar illite and K-feldspar dating

Olaf Brockamp [a,*], Norbert Clauer [b]

[a] Fachgebiet Mineralogie, Fachbereich 5 Geowissenschaften, Universität Bremen, Germany
[b] Laboratoire d'Hydrologie et de Géochimie de Strasbourg (CNRS-UdS), Université de Strasbourg, France

ARTICLE INFO

Article history:
Received 23 November 2012
Received in revised form 4 August 2013
Accepted 6 August 2013
Available online 17 August 2013

Editor: U. Brand

Keywords:
Lodève U-district
Permian sediments
Illite
K-feldspar
K–Ar dating
Wall-rock alteration

ABSTRACT

Mineralogical and chemical analyses combined with K–Ar dating of illite and K-feldspars were carried out on bulk samples and different fractions from Permian shales around the Lodève U-deposit to identify diagenetic and hydrothermal alteration episodes and their timing. Authigenic $2M_1$ and 1M illite with K–Ar ages between 270 and 245 Ma are the predominant mineral types in the shales. They are of early diagenetic origin relative to deposition and formed apparently directly from pyroclastic materials in a lagoonal to deltaic environment under semi-arid conditions. Albite and a first generation of K-feldspar developed by a replacement of analcime, the K-feldspar growing only in the former lagoonal environment that favored also early diagenetic dolomitization at the expense of calcite.

The hydrothermally altered shales next to the U-deposit contain authigenic quartz, Fe-chlorite, neoformed illite, and a second-generation K-feldspar with K–Ar ages beginning at about 220 Ma (Triassic), although Jurassic and Cretaceous ages were also obtained. This younger age spectrum (Jurassic/Cretaceous) is close to previous U–Pb isotope data from the U-deposit, probably reflecting several episodes of U-mobilization. Therefore, the hydrothermal activity extended episodically from Triassic to Cretaceous time within the U-deposit. The hydrothermal temperatures attained locally >220 °C as the K–Ar system of illite from early Permian diagenesis is partially reset. Triassic hot fluids ascended along faults into the northern area of the Lodève basin during an initial rifting of the nearby western Tethys Ocean. Further fluid pulses were recorded at Lodève during the opening of the North Atlantic and separation of Europe from Africa (Jurassic/Cretaceous), which also caused the peak hydrothermal activities in Central and Western Europe. As the Lodève area is located between two independently developing oceans it could have been supplied with hot fluids for a long period of time.

1. Introduction

Wall rocks of ore deposits are often hydrothermally altered and well known is the zoning pattern of porphyry copper deposits with a potassic central zone and phyllic and propylitic zones around (e.g. Evans, 1993). These features result from local chemical and/or thermal gradients and provide key information about origin and timing of these deposits. Likewise, alteration assemblages in sedimentary ore deposits may yield reliable information about their genesis and timing by dating isotopically reference minerals. For instance, illite from the central alteration zone of the Müllenbach U-mineralization in Permo-Carboniferous arkosic sandstones and shales of the Black Forest, Germany, yields a mean K–Ar age of 145 ± 4 Ma, which verifies, together with a high vitrinite reflectance, a Jurassic epigenetic mesothermal U concentration (Brockamp et al., 1987). This deposit was previously classified as an epigenetic sandstone U-deposit produced by flowing meteoric groundwater, with a weak roll front mineralization (Kneuper et al., 1977).

A logical consequence is, therefore, to study on a larger scale the U-mineralization Lodève (southern France) likewise bound to Permian sediments though consisting of high proportions of former pyroclastic material. Different interpretations have been attributed successively to both the origin of the Lodève U-deposit and the genesis of associated minerals from the Permian sediments deposited at the margin of the western Tethys Ocean. The ore minerals (pitchblende, coffinite with traces of PbS, ZnS, FeS_2) were described in either C_{org}-rich sediments or major bituminized faults. The mineralization was initially considered syn-diagenetic/early diagenetic (Comte et al., 1983), with some petrographic characteristics of the sedimentary pile. Thus albite and analcime (assumed to be authigenetic) are replaced downwards by K-feldspars (assumed to be detrital). Smectite was considered to be transformed into illite and calcite into dolomite during an advanced diagenetic stage. Conversely, Brockamp and Zuther (1986) concluded, after their first excursion to Lodève U-district in a report to J. Saint Martin at the

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* Corresponding author.Tel.: +49 421 218 65220.
E-mail address: michelse@uni-bremen.de (O. Brockamp).

0009-2541/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.chemgeo.2013.08.009

COGEMA office, Lodève in September 1986, that smectite in particular is lacking, and that K-feldspar seems to form an anomaly around the deposit. Preliminary illite K–Ar data indicated also younger ages within the deposit (197–240 Ma), while they increased to 240 to 250 Ma in the surrounding region (N. Clauer, unpublished data). Later Schneider et al. (2006) detailed likewise illite, K-feldspar and dolomite as typical minerals in the lower sequences, and illite, albite, analcime and calcite in the upper series with most minerals possibly formed by early diagenetic processes. U–Pb concordia diagrams of pitchblende pointed to a Permian primary U concentration (Lancelot and Vella, 1989), whereas whole rock U–Pb isotopic data and microthermometric measurements were interpreted as hydrothermal mineralization and/or remobilization events at about 180 and 100 Ma (Lancelot et al., 1984; Lancelot and Vella, 1989); this concept was also adopted by Mathis et al. (1990). Published illite K–Ar ages from U-bearing Autunian units even scatter between 250 and 100 Ma, with the younger ages resulting from local hydrothermal fluid migrations in faults, while the older ages were close to the sedimentation age (Mendez Santizo et al., 1991). Alternatively, Conrad et al. (1986) explained the decrease of K-feldspar K–Ar ages from 248 ± 8 to 173 ± 5 Ma from upper to lower Autunian units by a prograding diagenesis.

To resolve these apparent discrepancies in the evolution of the Lodève-U district, an improved knowledge about the changes in the mineral assemblage of the Permian sediments was needed to identify and characterize the varied modifications. The best approach was then a detailed and reliable identification of successive alteration zones. This study is focused on such mineralogical- and time-specific relationships. To address it, 270 samples were collected from the Lodève basin for mineral and chemical analyses, and of these, 37 samples were used for K–Ar analyses. From his archives N. Clauer contributed also 15 illite K–Ar data of Lodève area.

2. Geological setting

For definition and subdivision of the Permian sedimentation period in the Lodève basin, names of selected regional stages and formations were adopted from Mathis et al. (1990) and Gradstein et al. (2012). Accordingly the Lower Permian (Rotliegend) is divided from top to bottom into the Saxonian and Autunian, the latter composed upwards of the three following lithostratigraphic units and formations: Autunian gray (Usclas formation), Autunian red + gray (Loiras formation) and Autunian red (Mas d'Alary and Viala formation). The Saxonian stage consists of the Rabejac, Salagou and La Lieude formation. In the geological map 1:50,000 Lodève of Alabouvette et al. (1982) – on which the sample collection is located – the Saxonian is shown undivided and the Autunian subdivided into the three formations. For clarity reasons the termini of the lithostratigraphic units e.g. Autunian gray, Autunian red + gray, Autunian red and Saxonian were used here.

The Lodève Permian basin covers an area of 150 km^2 (Fig. 1) in the southeastern part of the Massif Central. The basin is bordered to the W, SE, and E by faults and Mesozoic limestones, and has a half-graben shape dipping with 10–15° to the S. The half-graben sediments overlie carbonates and schists of the Hercynian basement (1:50,000 geological map, Lodève of Alabouvette et al., 1982; de Joussineau et al., 2005). Basin sediments of the southern, deepest part are about 4000 m thick due to a significant subsidence along the Les Aires Fault. During uplift from upper Thuringian (upper Zechstein of Upper Permian) to middle Anisian (Middle Triassic), about 1500 m of the uppermost sediment filling of the basin was eroded, so that the Hercynian basement, the Permian basal conglomerates and the Autunian series crop out to the N. The sedimentary rock sequence of the Autunian is cut by a system of E–W striking faults, and hosts the U-deposit. The basement contains hydrothermal barite veins – occasionally with nacrite (Buatier et al., 1996) – that may be related potentially to the system of unconformity bound ore deposits of the Massif Central. Saxonian sediments are exposed to the S, whereas Triassic and Jurassic sediments were identified above an unconformity at the far southern end of the basin. These Triassic and Jurassic sediments are relics of a former 1000-m thick cover. Permian and Mesozoic sediments are locally capped by Pliocene basaltic flows.

According to Laversanne (1976) and Comte et al. (1983), the Autunian sediments above the basal conglomerate can be divided into three carbonate-rich units from bottom to top: a gray unit of about 150 m (Autunian gray), an alternating red and gray unit also of about 150 m (Autunian red + gray), and a red unit of about 300 m (Autunian red). The units consist of repetitive 0.5 to 2 m thick strata, each made up of three lithological sequences: (i) fine-grained sandstones at the base, which pass into (ii) C_{org}-rich silt and shales, sometimes bituminous, and (iii) pelites at the top. The chemical composition of the associated organic matter was investigated by Schlepp et al. (2001 with more landmark references). Twenty layers of pyroclastic materials, centimeter-to-decimeter-thick, are interbeded with the Autunian shales over a wide area. The Autunian sediments are unconformably covered by about 1700 m of carbonate rich, clay-dominated, red-colored Saxonian series that contain in addition 10 pyroclastic layers. Thus a continuous volcanic activity during Permian is verified, whereby the volcanic products developed from an early calc-alkaline to a latter alkaline type (Nmila et al., 1992; Schneider et al., 2006). Sediment deposition in the basin occurred at semi-arid and shallow-water conditions being initially lagoonal and later mostly deltaic derived. Climatic variations are more detailed by Schneider et al. (2006), while specific tectonic features in the basin are outlined by de Joussineau et al. (2005) and Wibberly et al. (2007).

3. Material and methods

A total of 98 samples were collected from outcrops of the different Permian stratigraphic units (including 15 from open pits), while 129 samples were taken from 7 boreholes and 12 from underground mine galleries. The samples are mainly of shale type. Fig. 2 shows the outcropping sites and the locations of the boreholes drilled mostly into the area of the E–W striking faults, where U concentrations were expected. As collection of samples followed the outlines of the geological map 1:50,000 Lodève (Alabouvette et al., 1982) with the Saxonian being undivided, its sequence is classified arbitrarily into two units (I and II) to facilitate handling of the data.

Examination of the samples was conducted in three successive steps:

1) Identification of the minerals by optical microscopic observation of thin sections, made from 71 samples distributed among the stratigraphic units as follows: Saxonian (2 samples), Autunian red (20 samples), Autunian red + gray (20 samples), Autunian gray (25 samples), and basement (4 samples).

2) Crushing of 20 g of each sample, of which 10 g was powdered for further mineralogical and chemical analyses. The remaining 10 g of 64 crushed samples was disaggregated in deionized water by ultrasonic treatment and the <2 μm fraction separated by centrifugation for clay mineral studies. Of the clay fractions, 10 are from Saxonian, 16 from Autunian red, 26 from Autunian red + gray, and 12 from Autunian gray units.

Quantitative chemical analyses of bulk rock samples and <2 μm fractions were carried out on pressed disks of micronized material with an electron microprobe enabling the analysis of minute amounts (50 mg). The rock powder was placed into cylindrical depressions (3 mm diameter, 1 mm deep) of a cellulose plate (40 mm diameter) and pressed under 500 bars with a polished steel piston (Zuther and Brockamp, 1988). The relative error of this analytical technique is comparable to that of X-ray fluorescence analysis (XRF) as correlation coefficients of 0.99 were obtained for XRF versus microprobe data for the contents of the major and minor elements of 26 samples from borehole MLV 345.