Multiple fluid infiltration contributed to the supergene Fe deposit at Petronell (Germany) – chronology of events by goethite and todorokite U-Pb dating

István Dunkl, Hilmar von Eynatten, Keno Lünsdorf
University of Göttingen, Germany
Proceedings of the 15th SGA Biennial Meeting, 27-30 August 2019, Glasgow, 909-911.

Abstract.

Goethite and todorokite were deposited alternately in fault-related impregnations in Lower Triassic sandstone along the rift shoulders of the Upper Rhinegraben (URG) in Germany. Laser ablation U-Pb dating of these minerals show two distinct age clusters: around 45 Ma (Mid-Eocene) and 4 to 2 Ma (Pliocene). The older ages suggest that the supergene mineralization occurred coevally with the early rifting phase of the URG, while the young ages are measured in subsequent mineralizations reflecting a late re-activation of the faults and related descendent, meteoric fluid flow.

1 History of mining

The former Petronell mining area is situated in the southern part of Rhineland Palatinate close to Bad Bergzabern. The so called "limonitic" ore was mined intermittently from around 1580 until the second half of the 19th century. From the subsurface mining activity at Petronell the yearly production was around 400 metric tons at the beginning of the 19th century (Walling, 2005). These relatively small deposits characterized by dominantly goethite impregnation of Triassic Bunter sandstone along local and regional faults are widespread in the region. Their former iron production contributed to the regional technological development from the 16th to the 19th century (e.g., Held and Günther 1993).

2 Geology of the region and formation of the deposit

The deposit is located at the western rift shoulder of the Upper Rhinegraben (URG) in the Palatinate Forest (Fig. 1). The URG extends in a NNE–SSW direction for about 300 km between Basel and Frankfurt, is over 30–50 km in width, and forms part of the European Cenozoic rift system (ECRIS; Ziegler and Dèzes 2005). The URG is bordered by more or less symmetrical, up to 1500 m high rift shoulders on its eastern and western sides; the maximum vertical throw between the base of the graben and the uplifted flanks exceeds 4 km. The rift shoulders expose the European basement (mostly Variscan granitoids and metamorphic rocks), Permian volcano-sedimentary sequences, and Mesozoic epicontinental deposits.

Rifting of the Upper Rhinegraben was initiated in mid-Eocene time at around 47 Ma (Illies 1977; Grimmer et al. 2017). The extension occurred in several pulses with contrasting mechanisms. The basin fill records the associated major subsidence phases at around 37–31 Ma, 25–18 Ma and post-5 Ma. Mafic alkaline volcanism has been associated with the development of extensional structures in and around the graben system (for a brief summary on the evolution see Walter et al. 2018).

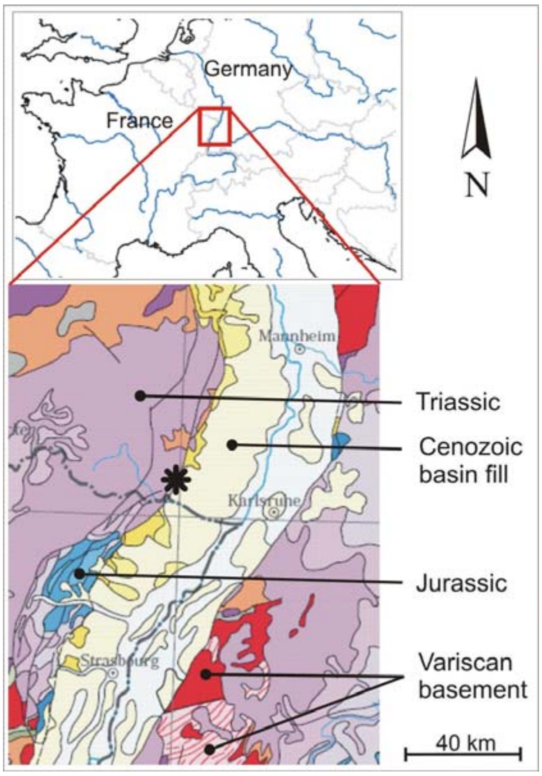

Figure 1. Geological sketch map of the Upper Rhinegraben (map base: Geological map of Germany, 2 mio, BGR, Hannover, 2004). Star indicates the Petronell deposit situated along the western main boundary fault of the URG.

The goethite impregnations form irregular, partly fault-related bodies in the Lower Triassic Bunter sandstone. The most plausible mechanism for the mobilisation and supergene precipitation of iron assumes a gravity-triggered flow cell that developed following the formation of the fault-controlled relief along the rift shoulder. Potentially Cenozoic lakes and swamps may have developed in the rift valley during the early extensional phase and may have reduced the pH of the infiltrating meteoric water, enhancing the removal of iron from the ferrous cement of the sandstones. The basal strata of the Cenozoic basin fill contains organic-bearing layers (Böcker and Littke 2016), thus assuming their former, wider extent above the current rift shoulders is a reliable scenario.

3 Mineralogy and geochemistry

The mineral phases were identified by Raman spectroscopy using 532 nm wavelength laser light, while their chemical composition was determined by laser ablation using an excimer laser and an Element2 ICP mass spectrometer. Laser ablation line analyses were performed in order (i) to characterize the composition of the minerals and zones of the ore, and (ii) to demarcate potential minerals and/or zones where the concentration of U and the Pb/U ratio is appropriate for U-Pb geochronology. The applied spot size was 75 µm (speed: 20 µm/s) and 54 analyses were registered from 46 elements.

The dominant mineral of the Fe-ore is goethite, forming tight impregnations and partly botryoidal crusts in the fissures of the sandstone. The composition of the goethite in the botryoidal crust shows a gradual change from the early layers towards outer layers precipitated later (Fig. 2). The internal zone is richer in trace elements, including increased Al->Fe substitution in goethite. The uranium concentration is typically constant, but in some samples it shows a 3-fold increase towards the younger goethite layers (i.e. towards the rim). In these external zones the Pb/U ratio and the U concentration are appropriate for the application of U-Pb geochronology.

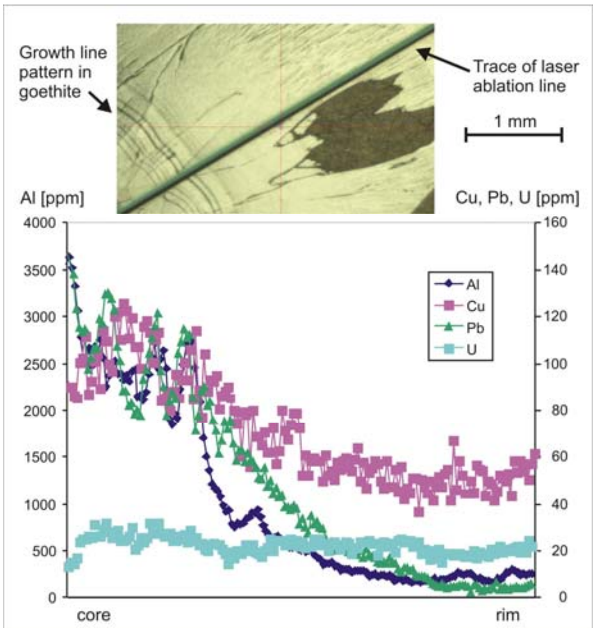

Figure 2. Concentration of some trace elements in a thin goethite crust from the Petronell mine. Laser ablation line analysis along a ca. 4 mm long section (reflected light microscopic image in the upper panel).

Todorokite and pyrolusite are the typical Mn-minerals in the deposit, but they occur in smaller amounts than goethite. The textural context of the Fe- and Mn-minerals is not obvious, sometimes the Mn-oxide phases are older than the main goethite phase, but also younger Mn-oxide generations can be recognised. Oscillating fluid conditions cannot be excluded. The Mn-oxide crusts are rather heterogeneous, exhibiting locally high porosity, and, in some minor cavities, mm-sized euhedral pyrolusite crystals. The goethite content in the Mn-oxide zones is variable. The Al content correlates well with the Fe content, but their ratio varies in different domains. Because Al shows no correlation with Si or K, it is likely that Al is incorporated in the lattice of goethite (Fig. 3).

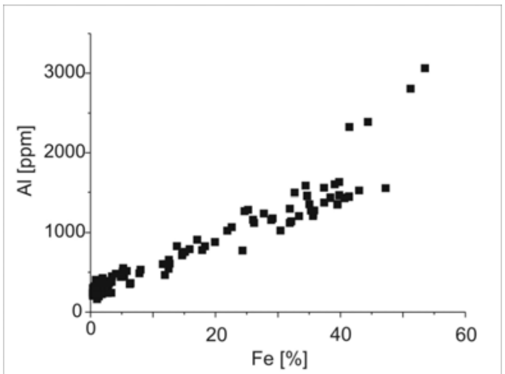

Figure 3. Correlation of Al and Fe in the zones of the ore with varying goethite content. The Al/Fe ratio varies between the zones.

4 Unconventional U-Pb dating using goethite and todorokite

The laser ablation analyses were performed using spot sizes between 33 and 90 µm. As no matrix matched any Fe-oxyhydroxide and Mn-oxide reference materials available for U-Pb geochronology, we used the most commonly used zircon reference materials (GJ1, Plesovice, 91500 and FC1) for fractionation and drift correction. The ablation behaviour of these reference materials differs from the metal(oxy-)hydroxides, but the bias introduced by this contrast should be less than 10%. The samples contain highly variable amounts of common lead, so the ages were calculated as lower intercepts on the Tera-Wasserburg plot.

We recorded two age groups in the todorokite phases: (i) around 45 Ma (Mid-Eocene) and around 4 to 2 Ma (Pliocene). For the goethite it was possible to date only the outer zone of the crusts, as only in this thin layer was the Pb/U ratio acceptable for geochronology (Fig. 4). These spots yield Pliocene ages, similar to the younger age group detected in the Mn-oxides.

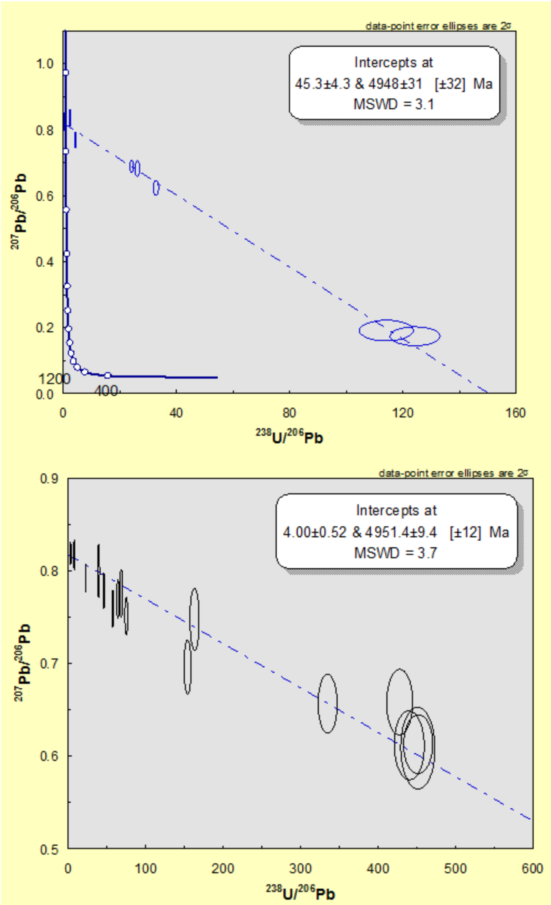

Figure 4. Upper panel: Tera-Wasserburg plot of a typical Eocene U-Pb age determined in the early generation of todorokite. Lower panel: Pliocene U-Pb age measured on the external layer of the botryoidal goethite.

5 Conclusions

- The two age groups are well characterised, with very few ages in between these two groups.
- The coherent Pliocene ages detected in different phases indicate that the U-Pb system remained closed after the formation of these minerals. We therefore interpret these data as well-defined temporal constraints on fluid movement (i.e. hydrochronology).
- The older ages match the opening of the Upper Rhinegraben and indicate that the descendent, oxidative meteoric water had reached the currently exposed level of Lower Triassic sandstone by the Mid-Eocene, in the early period of rifting.
- The younger ages coincide well with the youngest, <5 Ma subsidence phase in the Upper Rhinegraben. Probably the associated faulting opened older fissures and generated renewed descendent water circulation leading to the precipitation of the young goethite and todorokite generations.
- So far no ore specimens have yielded Miocene U-Pb ages that are characteristic of fissure-filling carbonates in the Schwarzwald ore district, at the southeastern rift shoulder of the Upper Rhinegraben. This might be due to (i) the small sample numbers (i.e. statistical reason), or (ii) the lack of volcanic activity in the region in contrast to the southern URG.

Acknowledgements

Many thanks to Wolf-Gerd Frey for providing samples from Petronell.

References

Böcker J, Littke R (2016) Thermal maturity and petroleum kitchen areas of Liassic Black Shales (Lower Jurassic) in the central Upper Rhinegraben, Germany. International Journal of Earth Sciences, 105, 611–636.

Grimmer JC, Ritter JRR, Eisbacher GH, Fielitz W (2017) The Late Variscan control on the location and asymmetry of the Upper Rhinegraben. International Journal of Earth Sciences, 106, 827–853.

Held UC, Günther MA (1993) Geologie und Tektonik der Eisenerzlagerstätte Nothweiler am Westrand des Oberrheingrabens. Jahresberichte und Mitteilungen des Oberrheinischen Geologischen VEreins, N.F., 75, 197–215.

Illies JH (1977) Ancient and recent rifting in the Rhinegraben. Geologie en Mijnbouw, 56:329–350.

Walling H (2005) Der Erzbergbau in der Pfalz : von seinen Anfängen bis zu seinem Ende. Landesamt für Geologie und Bergbau Rheinland-Pfalz, 228 p, Mainz.

Walter BF, Gerdes A, Kleinhanns IC, Dunkl I, von Eynatten H, Kreissl S, Markl G (2018) The connection between hydrothermal fluids, mineralization, tectonics and magmatism in a continental rift setting: Fluorite Sm-Nd and hematite and carbonates U-Pb geochronology from the Rhinegraben in SW Germany. Geochimica et Cosmochimica Acta, 240:11–42.

Ziegler PA, Dézes P (2005) Evolution of the lithosphere in the area of the Rhine Rift System. International Journal of Earth Sciences, 94 594–614.