Denitrification potential and occurrence of reactive minerals in a fractured carbonate aquifer (Upper Muschelkalk)

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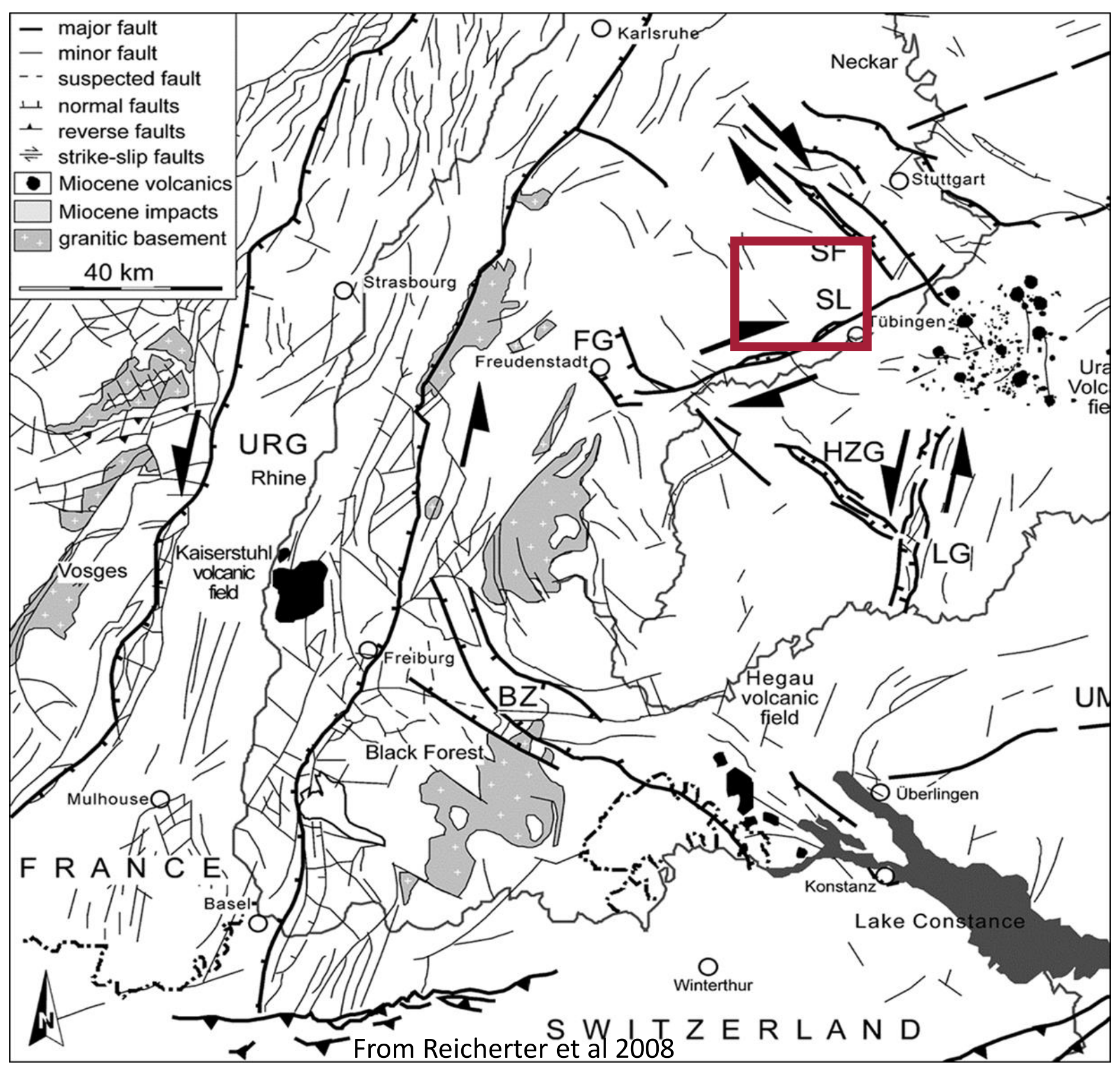
Introduction

Fractured or karstified carbonate rocks constitute major drinking water resources. Nitrate is one of the major threads for drinking water suppliers in regions with intensive agricultural use. Field scale observations in the Upper Muschelkalk aquifer in the “Oberes Gäu”, SW-Germany, suggest that denitrification due to oxidation of Fe(ll)- or sulfide-bearing minerals might be an important attenuation process at least in cases of extended mean residence times of waters (> 5-40 y).



From Reicherter et al 2008

Materials and methods

To identify reactive minerals within the rock matrix, samples have been taken from major facies types within the Upper Muschelkalk. Samples have been analyzed in polished thin sections by transmitted (TL) & reflected light (RL) microscopy as well as electron microscopy (TEM) including energy-dispersive elemental analysis (EDX).

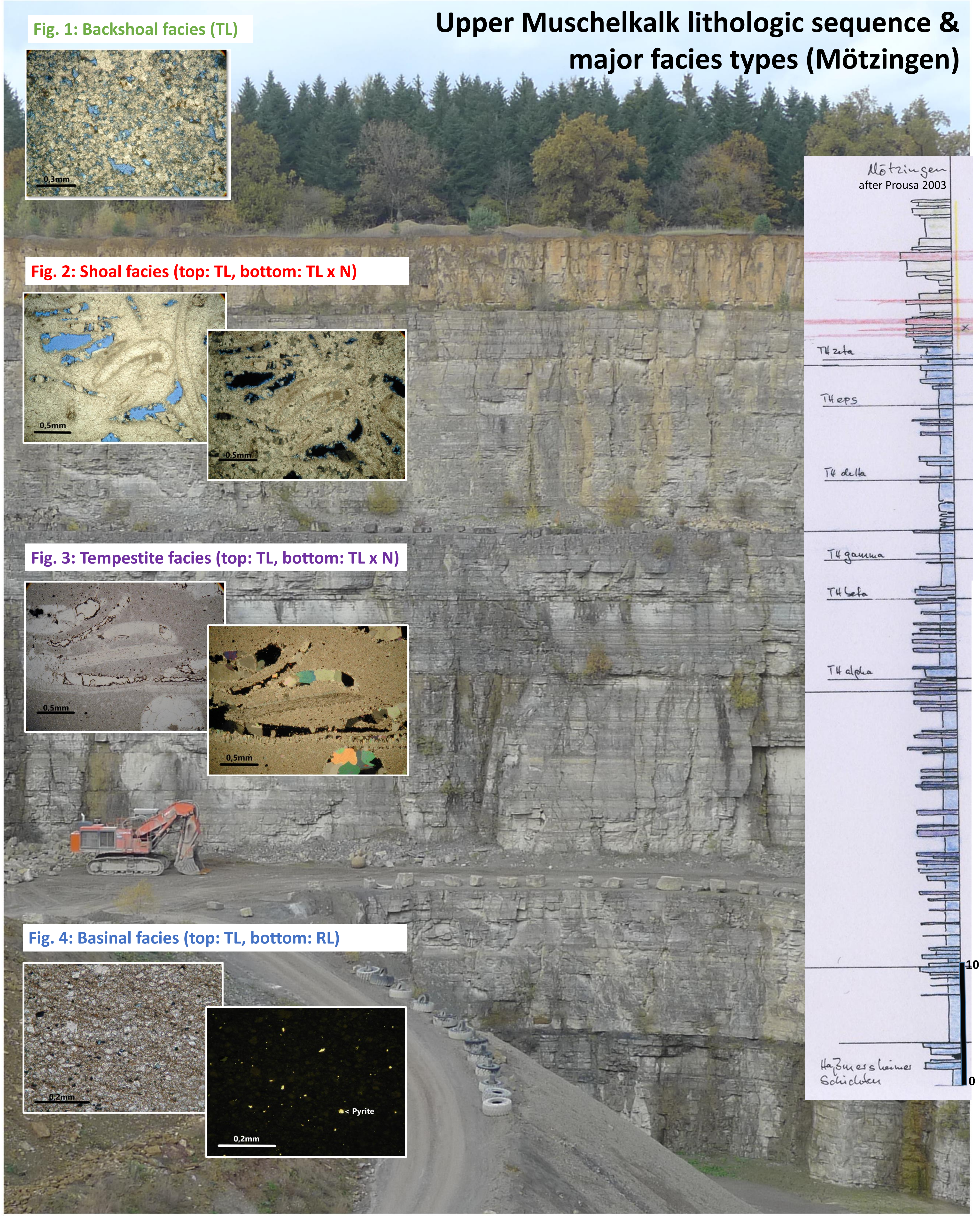

Upper Muschelkalk lithologic sequence & major facies types (Mötzingen)

Fig. 1: Backshoal facies (TL)

Fig. 2: Shoal facies (top: TL, bottom: TL x N)

Fig. 3: Tempestite facies (top: TL, bottom: TL x N)

Fig. 4: Basinal facies (top: TL, bottom: RL)

Facies types and reactive minerals

Major facies types are the mainly dolomitic backshoal facies (Fig. 1) at the top and the micritic basinal facies (Fig. 4) predominating in the lower part of the section. Shoal bodies (submarine carbonate sand accumulations; Fig. 2) are more frequent in the upper part of the sequence. Tempestites (layers of carbonate storm deposits; Fig.3) are intercalated in the lower part. The latter two have thicknesses in the cm/dm-range.

Reactive Fe(II)- and sulfide-bearing minerals are pyrite (PY) – as synsedimentary and diagenetically formed minerals – and pyrite/marcasite as tectonically induced precipitations from low-T hydrothermal brines. Saddle dolomite (SD, Fe-bearing dolomite of probably also hydrothermal origin) precipitated in porous carbonates (Figs. 5-10). Concentrations of these minerals depend on facies types and amount to several weight percent iron. Porosities range from very low values (<1%) in micritic limestones to up to 25% in dolomites (see Table 1).

Table 1: Main parameters of the facies types (estimated from thin sections)

Facies	Lithology	Sedimentary environment	Porosity	Pore size diameter max/average	PY Vol%	SD Vol%	Size of minerals max/ average
Backshoal facies	laminated dolo-mudstones, burrowed dolomitic mudstones, massive dolomitic wacke- to packstones	coastal to lagoonal setting	15-28%	280 µm 114 µm	0-0,5%	0-1%	---
Shoal facies dolomitic/ calcareous	bioclastic (brachiopods, bivalves and skeletal debris) and oolithic dolomitic and calcareous grainstones	shoal body	dolomitic 20-30% calc. 15-20%	1,72 mm 0,8 mm	0,5-1% 0,5-1%	0-2% 0-2%	SD 1,5 mm/ 1,2 mm
Tempestite facies	graded packstones to wackestones with abundant skeletal debris, crinoidal columnar plates, lithoclasts	storm deposits of the mid- to deeper ramp	0,5-10%	1,52 mm 0,5 mm	0,5-1%	0-2%	SD 1,28 mm/ 0,76 mm
Basinal facies	dark grey, well bedded or nodular micritic limestones and marlstones with intercalated thin marlstone drapes	basinal setting below/around storm wave base	0,5-5%	n.d.	up to 2%	0-0,5%	PY 40 µm/ 17,5 µm

Fig. 5: Saddle dolomite in shoal facies, TL and TL x N

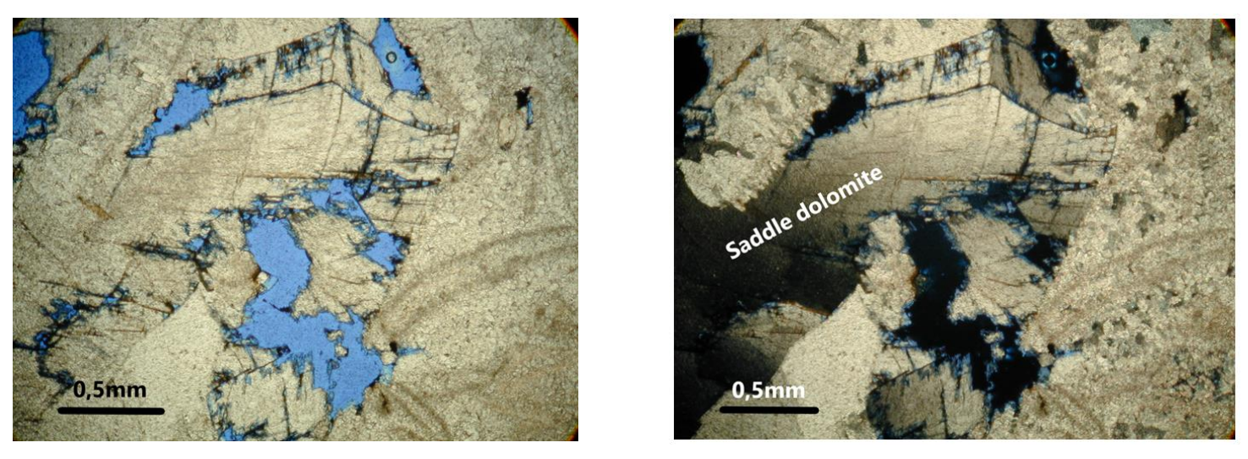


Fig. 6: Saddle dolomite in tempestite facies, TL and TL x N

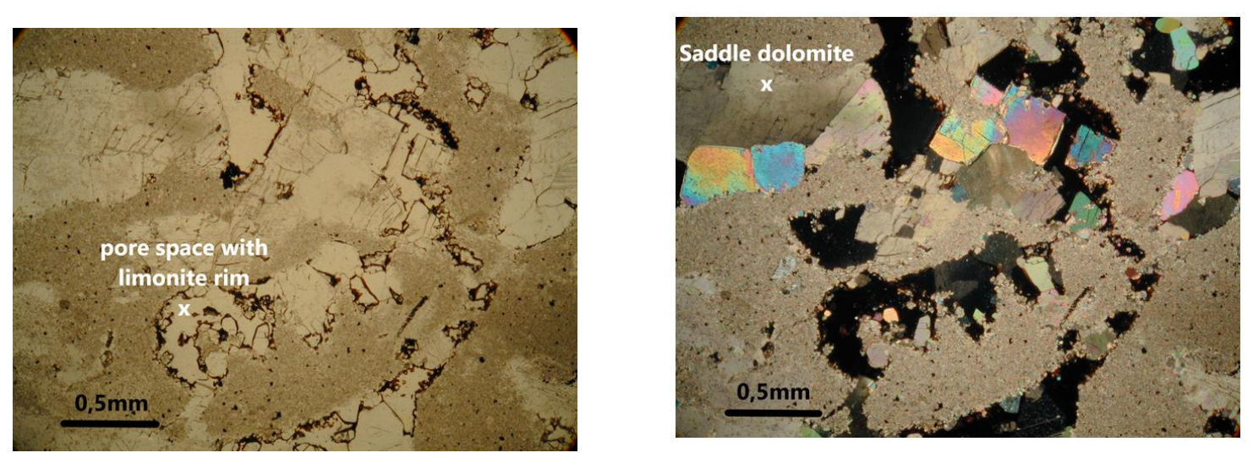


Fig. 7: Saddle dolomite in fracture, TL and TL x N

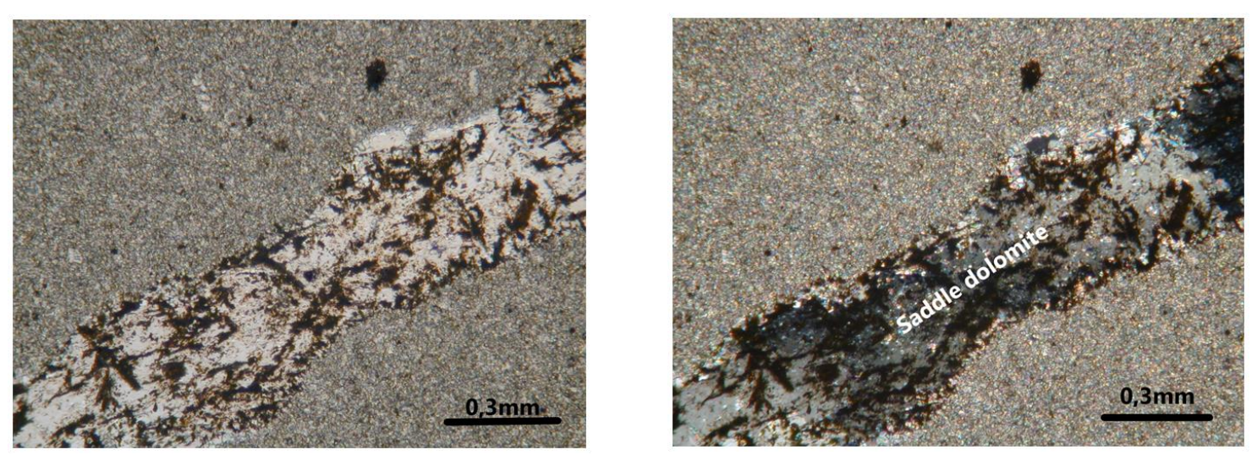


Fig. 10: Pyrite and saddle dolomite in tempestite facies, edx microscopy

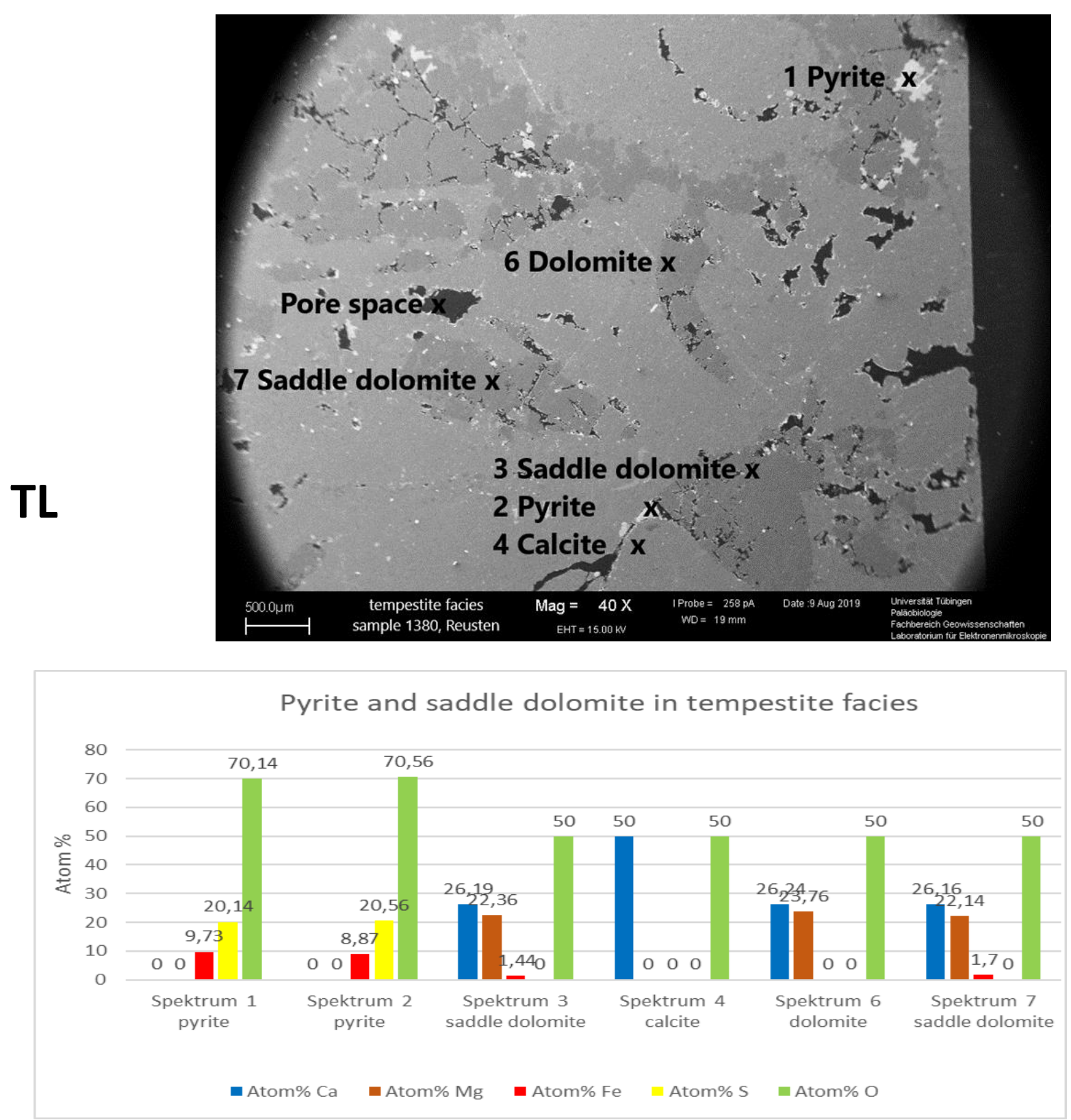


Fig. 8: Pyrite in basinal facies, RL

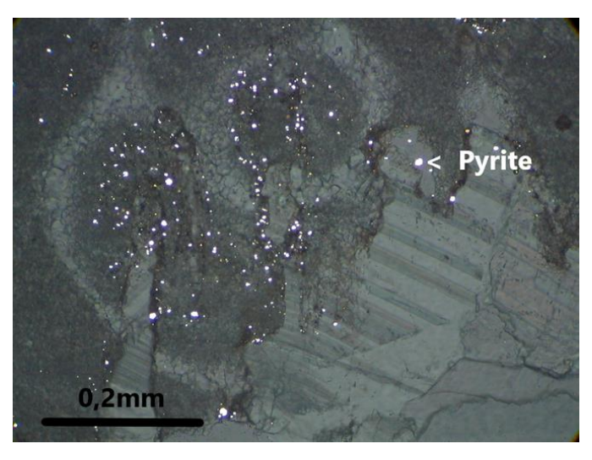
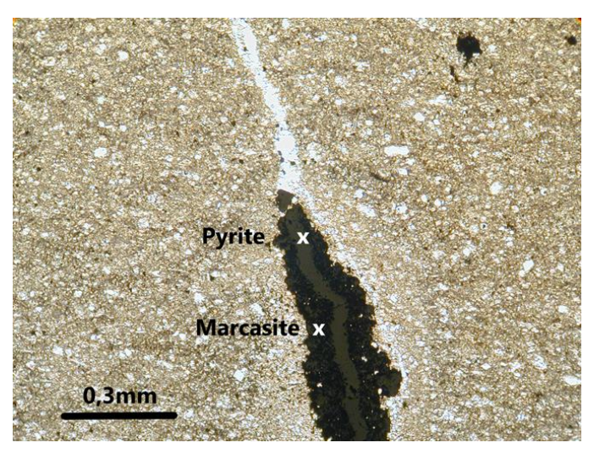


Fig. 9: Pyrite in fracture, TL



Conclusions

In combination with a hydrogeological characterization, these investigations allowed to delineate reactive zones within the fractured aquifer. Denitrification within these reactive zones depends on the amount and dissolution of these minerals as well as effective diffusion in the pore space.

Acknowledgement: This work was supported by the Collaborative Research Center 1253 CAMPOS (P5: Fractured Aquifers), funded by the German Research Foundation (DFG, Grant Agreement SFB 1253/1 2017).

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