Zeitschrift: Eclogae Geologicae Helvetiae

Herausgeber: Schweizerische Geologische Gesellschaft

Band: 74 (1981)

Heft: 1

Artikel: Some geochemical data on stylolites and their host rocks

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DOI: https://doi.org/10.5169/seals-165100

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Some geochemical data on stylolites and their host rocks

By Hans W. Schwander, Alfred Bürgin and Willem B. Stern¹)

ABSTRACT

Quantitative chemical analyses of stylolitic fillings and their host rocks (back-reef limestones of Kimmeridgian age from the Swiss Jura Mountains) indicate that Ca, and partially Mg have been dissolved, thus leading to an enrichment process of clay minerals, quartz, K-feldspar and pyrite. All stylolites examined so far contain calcite (microprobe, X-ray diffraction results); from the calcite content of stylolite versus host rock the amount of depletion by pressure solution may become estimated, if the initial carbonate rock is considered as homogeneous, and if solely a mobility of soluble elements is assumed. In an actual case a loss of approximatively 6% was found, being somewhat lower than reported literature values.

ZUSAMMENFASSUNG

Aus der chemischen Zusammensetzung von Stylolithenfüllungen und deren Nebengesteinen lassen sich genetische Informationen ableiten, falls von homogenen Ausgangsgesteinen und von ausschliesslicher Mobilität der löslichen Komponenten ausgegangen werden darf. Durch Drucklösung infolge diagenetischer oder tektonischer Prozesse werden Kalzit und teilweise auch dolomitischer Kalzit aus dem Wirtsgestein entfernt, wobei sich unlösliche Komponenten wie Quarz, Kalifeldspat, Tonmineralien, Pyrit anreichern und sich Stylolithensäume bilden. Diese sind in den untersuchten Fällen nie frei von Kalzit, so dass der Anreicherungs- bzw. Lösungsfaktor beispielsweise nicht direkt aus dem Quarz- oder Tongehalt von Stylolith und Nebengestein abgeleitet werden kann. Vielmehr ist es notwendig, aus dem Kalzitgehalt von Stylolith bzw. Nebengestein eine Grösse zu ermitteln, die bei bekanntem Stylolithenanteil im Gesteinsaufschluss eine Abschätzung der gelösten Komponenten und damit der Volumenreduktion infolge Drucklösung ermöglicht. Diese Reduktion berechnet sich in einem konkreten Fall auf rund 6%, die grössenordnungsmässig zwar in Übereinstimmung mit Literaturwerten, aber tendenziell tiefer ist. Anhand von vier Fällen wird die Möglichkeit einer geochemischen Massenbilanz kurz diskutiert, wobei auf einschränkende Voraussetzungen gesondert eingegangen wird.

Introduction

If we follow the stylolite definition of the "Glossary of Geology" (1977), most of the irregularly shaped seams occurring in limestones of the Jura Mountains have to be interpreted as stylolites. Though this term is mainly used in a descriptive sense, an either diagenetic, or tectonic pressure solution is assumed to be the driving force of stylolite formation.

A recent bibliography (compiled by the Lamont-Doherty Geological Observation 1980) shows a growing interest in pressure solution phenomena; however, no attempts seem to have been made so far to study mass balances connected with stylolite genesis by means of quantitative chemical analyses of stylolitic seams.

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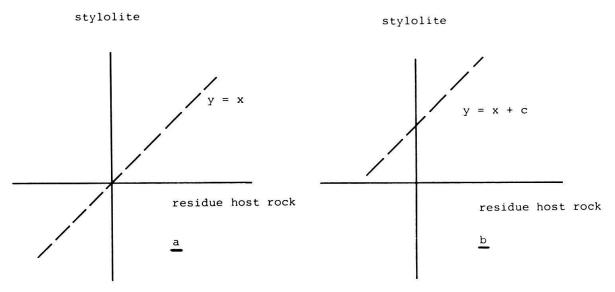


Fig. 1. Projection points of elemental ratios containing solubles (a), and solubles + insolubles (b) (logarithmic scale).

Some authors (STOCKDALE 1926; BODOU 1976) tried to calculate the volume reduction connected with stylolitization by forming ratios of clay minerals of host rock vs clay minerals of stylolites, assuming calcite-free stylolites.

Since, however, stylolites in carbonate rocks contain considerable amounts of calcite, these data tend to give volume reduction rates which are too high.

If a given, more or less homogeneous rock volume consisting of an insoluble part A (e.g. clay-, detritic minerals) and a soluble B (e.g. calcite, dolomitic calcite) undergoes pressure solution, a loss of volume with or without compaction, as well as an enrichment of insoluble parts have to be expected. Residual seams, originated by this mechanism, may contain the same minerals as the adjacent host rock, but in different amounts, if part of the soluble matter has been removed. In any case, elemental ratios of insoluble elements (A: Si, Al, Fe, K, Ti) to be found in host rock and residual seams must under these premises show identical values (Fig. 1a).

If, however, the ratio contains a soluble (B: Ca, \pm Mg), or partially soluble element, the values thus obtained must not be any more identical (Fig. 1b).

A broad scatter of elemental ratios may be expected, when

- the original rock volume has been heterogeneous (e.g. primarily banded),
- the seam material did not originate in situ, but has been transported from somewhere else to its present location,
- the analytical data are too inacurate.

In a first attempt (1975-80), X-ray diffraction and chemical analyses (X-ray fluorescence, electron microprobe) on stylolite fillings and adjacent host rocks were carried out in order to check

- which element can be regarded as soluble or insoluble,
- what minerals are involved in depletion/enrichment processes,
- what rock volumes have to be dissolved to obtain the present stylolitic seams.

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Sample material

The specimens are taken from the Reuchenette Formation (back-reef limestones, lower Kimmeridgian) exposed in a small E-W striking anticline within the tabular Jura near Porrentruy (Canton Jura, Switzerland) in the northern foreland of the folded Jura. The beds dip 12° to the north.

The lithology of all samples is a mudstone, the dominant rock type of this formation. The color of the samples, taken from natural outcrops varies from light yellow to tan; fresh samples of layers exposed in new road cuts and quarries are bluegreyish.

The columns of the stylolites are oriented perpendicularly to the bedding plane and are therefore interpreted as "stratigraphic" or "diagenetic" stylolites. Thus, stylolitization took place after lithification and predated folding.

Sample preparation, analytical data

Stylolite-free parts of host rocks, adjacent to stylolitic seams, were removed by sawing and prepared by crushing in a tungsten carbide disc mill. The dried, powdered sample was weighed, treated with acetic acid for 24 hours, washed, dried and weighed again.

Stylolite fillings were cautiously scratched out with a spatula avoiding contamination with host rock material, dried and weighed again.

Samples for wavelength dispersive X-ray fluorescence ("WDS-XRF") were treated according to STERN (1979). The usual sample weight was 150 mg, but in certain cases less than 20 mg were obtained; thus, analytical data were recalculated to 150 mg sample weight.

In a few cases, surfaces of adjacent host rocks were directly analyzed by energy dispersive X-ray fluorescence ("EDS-XRF"; the irradiated surface being 3×3 mm; calibration with synthetic reference samples).

For electron microprobe analysis, the specimen containing stylolitic material together with host rock was cut, polished and coated with carbon; for details see SCHWANDER et al. (1980).

Carbon oxide was determined by solution with HCl and titration with NaOH using phenol-phthaleine as an indicator.

The analytical data on bulk chemistry of stylolitic seams and adjacent host rocks are presented on Table 1, the microprobe analyses of individual mineral grains follow on Table 2.

Results

X-ray diffractometrial and electron microprobe results prove that the analyzed Kimmeridge samples – host rocks and stylolite fillings as well – contain calcite, quartz, clay minerals, K-feldspars, dolomite, pyrite: a composition corresponding with investigations published by SCHOT et al. (1970).

After treatment with acetic acid, most of the host rock samples still contain a slight calcite content, as the determination of CO₂ proves. On the other hand, stylolite fillings have considerable calcite contents – the latter not being due to preparational shortcomings, but due to the mineralogy of stylolitic seams, as microprobe results prove clearly. As a consequence, it is not possible to calculate an enrichment or depletion factor simply by forming elemental ratios of e.g. Si or Ti.

The insoluble part consists of several minerals, including some complex species and therefore being rather difficult to analyze especially in stylolites, it is preferable to use the calcite content for an indirect determination of the insolubles defining the depletion D as

100 · (100 - calcite_{host rock})/(100 - calcite_{stylolite}).

Table 1: Bulk chemistry of stylolites and their host rocks (XRF).

specimen		host rock residue	host rock	EDS	B yellow stylolite	host rock residue	host rock recalc.	EDS
sample	XV 4564	XV 4573+		Al	XV 4565	XV 4571+		B 5
Fe ₂ O ₃ MgO CaO K ₂ O TiO ₂ SO ₃ OO ₂	18.8 7.4 2.5 1.3 36.6 1.4 .30 .52 28.3	56.2 18.0 5.7 1.5 .9 3.1 1.27	1.3 .4 .1 .0 54.7 .1 .03	1.7 .4 .3 .0 54.7 .0 .03 .1 42.9*	27.4 11.9 7.0 .8 24.6 2.7 .80 .5	54.3 19.6 7.1 1.7 .8 3.6 1.10	1.4 .5 .2 .0 54.6 .1 .0	1.7 .0 .3 .0 52.0 .0 .0 .1 40.8*
н ₂ о	2.8	12.2	.3		4.5	9.8	.3	
sum	99.22	99.57	100.23		99.2	98.5	100.0	
% ccite % depl.	64.3 5.6		98.0		43.2 4.4		97.5	
ppm Cr Mn	240 290	125			250			
Zn Rb Sr Zr	140	50 340 100 300			50 260 60 320			

speciment sample	D yellow stylolite XV 4568	VI.	host roc recalc.	k host rock EDS D 9	F grey, stylolite XV 4562+	host roc residue	k host roc recalc.	kh.r. EDS F8
SiO ₂ Al ₂ O ₃	18.0 7.5 6.2 .4 35.3 1.3 .49 .56 27.0 2.7	48.3 15.8 6.9 1.6 3.8 2.7 .91	.5 .2 .1 .0 55.4 .0 .01	.9 .0 .1 .0 54.0 .0 .00 .2 42.4*	17.4 5.7 1.7 3.3 37.3 1.0 .25 .31 29.1 3.9	48.8 16.2 4.9 3.1 5.0 3.3 .88	2.8 .9 .3 .2 53.5 .2 .05 42.0	3.7 .6 1.2 .0 52.2 .0 .00 1.3 41.0*
sum	99.45	98.71	99.91		99.96	98.87	100.75	
% ccite % depl.	61.4 3.1		98.8		66.1 14.8		95.0	
ppm Cr Mn Zn Rb Sr Zr		100 360 140 70 320			50 160 50 200 130 200	50 260 80 190		

explanations: residue = host rock material after treatment with acetic acid

recalc. = host rock, recalculated from residue

= direct surface analysis by energy dispersive XRF

% ccite = calculated calcite content (from CaO, CO_2) % depl. = calculated depletion: 100 · (100-Cchost rock) / 100-Ccstylolite * = recalculated CO_2 content (from CaCO₃)

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The total volume reduction R has then to consider the percentage of stylolitic surfaces in a given outcrop V(Fig. 2).

$$R = V \cdot \left(\frac{100 - \text{calcite}_{\text{stylolite}}}{100 - \text{calcite}_{\text{host rock}}} - 1 \right).$$

Table 2: Mineral analyses, electron microprobe, on specimen F. $HR = host \ rock$, $St = stylolitic \ filling$.

	Quartz		K-feldspar		Clay minerals		Pyrite		Calcite	Dolomite	
	HR	St	HR	St	HR	St	HR	St	St	St	St
SiO ₂	98.2	99.0	62.0	64.2	27.1	29.5	1.1	. 4	.0	1.1	1.5
Al ₂ O ₃	.3	.0	17.3	18.0	23.0	25.1	.0	.0	.2	. 4	.9
FeO _{total}	.1	. 2	.2	.1	1.0	1.0	51.4	45.0	.1	. 2	.6
MgO	.0	.1	.1	.0	.8	.8	.7	. 2	.9	20.2	19.1
CaO	. 4	.1	.8	.6	18.8	16.8	5.5	1.2	57.9	32.6	32.4
Na ₂ O	.0	.0	.2	.0	. 2	. 2	.0	.0	.0	.1	.1
K ₂ 0	.1	.0	16.1	17.3	5.7	5.7	.1	.1	.0	.1	. 2
TiO ₂	.0	.0	.0	.1	.1	.3	.0	.0	.0	.1	.0
so ₃	.0	.0	.0	. 0	.1	.0	41.2	50.7	.0	.1	.6

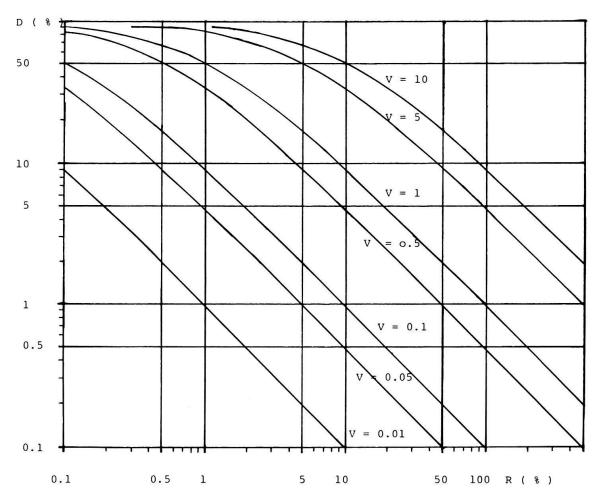


Fig. 2. Depletion *D* vs volume reduction *R*. V = % stylolite surface in outcrop $D = 100 \left(\frac{100 - \text{soluble}_{\text{host rock}}}{100 - \text{soluble}_{\text{stylolite}}} \right) \qquad R = V \left(\frac{100}{D} - 1 \right)$

The values D thus obtained vary between 3 and 15%; in no case calcite-free stylolites were observed. It follows – under the premises mentioned initially – that in a rock outcrop containing e.g. 0.5% stylolite surface and having a depletion factor of

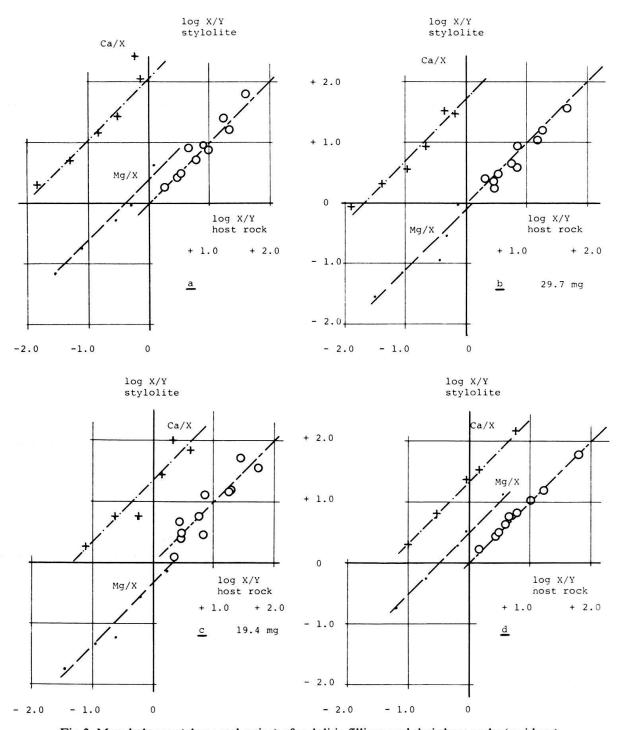


Fig. 3. Mass balances (elemental ratios) of stylolitic fillings and their host rocks (residues).

$$Insolubles (X/Y): \frac{Si}{Al} \frac{Si}{Fe} - \frac{Si}{K} \frac{Si}{Ti} \frac{Al}{Fe} \frac{Al}{K} \frac{Al}{Ti} \frac{Fe}{K} \frac{Fe}{Ti}$$

$$Solubles (Ca/X, Mg/X): \frac{Ca}{Si} \frac{Ca}{Al} \frac{Ca}{Fe} \frac{Ca}{K} \frac{Ca}{Ti} \frac{Mg}{Si} \frac{Mg}{Al} \frac{Mg}{Fe} \frac{Mg}{K} \frac{Mg}{Ti}$$

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20%, approximately 2% of the whole rock would have been dissolved (Fig. 2). This value would decrease when soluble B would recrystallize in the adjacent host rock. Since no porosity differences can be seen between adjacent and more distant parts, this effect is negligible at least in the cases discussed above.

The chemical data on bulk chemistry of stylolites and the insoluble residue of their host rocks (after treatment with acetic acid, Table 1) indicate that ratios containing insoluble elements only (Si, Al, Fe, K, Ti) plot on a straight correlation line passing through zero of the coordinate system. Ratios containing Ca as a soluble element in the numerator, plot – as expected – far beside the above mentioned correlation line (Fig. 3a-d), whereas Mg behaves somewhat differently: it may behave like an insoluble element (Fig. 3b, c), or like Ca as a soluble one (Fig. 3a, d).

In one case (Fig. 3c, specimen D) there is a considerable scatter of the projection points around the regression line. At least two reasons could be considered:

- the initial carbonate rock was inhomogeneous (see p. 218),
- the analytical error of this peculiar case is higher than the others.

Since specimen D only produced less than 20 mg stylolite material, the analytical error is higher than in cases where the normal amount of 150 mg was analyzed.

Finally, the volume reduction is estimated on specimen F. In a 10 by 10 cm area (thickness of layer = 10 cm), a stylolite surface of 110 mm² is found i.e. 1.1%. Taking a depletion factor of 15% from Table 1 and using nomogram of Figure 2, there results a volume reduction of approximately 6%, which is lower than reported literature values (BODOU 1976, STOCKDALE 1926).

Conclusions

The four studied stylolites/host rocks indicate that a close geochemical relationship exists between elemental ratios of insoluble chemical main constituents of stylolite fillings and their host rocks; the corresponding projection points plot on straight correlation lines passing through zero. The elemental and mineral content of stylolites correspond with that of the adjacent host rocks; the mode, however, is different – the respective mineral fractions vary. Nevertheless, the entire mass balance – as far as main constituents are concerned (trace elements have to be examined in a separate study) – may be explained by removing the soluble, or partially soluble elements, like Ca and Mg.

Elemental ratios containing a soluble element like Ca, or partially soluble like Mg, plot on parallel lines, as must be expected.

If the stylolites investigated so far originated from an initial homogeneous carbonate rock by pressure solution, and if only soluble elements were dissolved and removed, the depletion D permits an estimation of the volume reduction due to pressure solution, provided that dissolved elements did not recrystallize in the pore volumes of the adjacent host rocks. Since calcite-filled openings (veins, joints) seem to be connected with stylolite-bearing formations – a phenomenon which has to be studied in detail –, and since the pore volume does not seem to change from host rock fractions adjacent to stylolites to more distant parts, the above mentioned $CaCO_3$ -ratio together with the known stylolite percentage in a given outcrop allows an estimation of the upper limit of volume reduction due to pressure solution.

Using nomogram Figure 2, an actual case (specimen F) gave a volume reduction of 6% approximately.

The resulting amounts of volume reduction are lower than comparable values reported in literature, because the calcite content of a stylolitic seam reduces the volume percentage of the insoluble residue from a 100% to 100% minus volume percentage of calcite, a fact neglected by e.g. STOCKDALE (1926), BODOU (1976).

A further correction might be possible as soon as results on the source/sources of calcite occurring in stylolites (with their problems of kinetics and kinematics) are available – an investigation which is planned for further study.

Acknowledgment

The authors wish to thank Mrs Lusser for reading the manuscript.

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