DIAGENESIS AND PORE STRUCTURE OF THE "REGENSBURGER GRÜNSANDSTEIN" - BASE OF ITS TECHNICAL PROPERTIES

DIAGENESE UND PORENRAUM DES REGENSBURGER GRÜNSANDSTEINS - GRUNDLAGE SEINER TECHNISCHEN EIGENSCHAFTEN

DIAGENESE ET STRUCTURE DE PORE DU "REGENSBURGER GRÜNSANDSTEIN" - BASE DE SES PROPRIETES TECHNIQUES

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ABSTRACT

Three varieties of the glauconitic "Regensburger Grünsandstein" were revealed by petrographical, geochemical, and pore structure analysis of unweathered drilling cores from the Cathedral of Regensburg and from the "Alte Pinakothek" in Munich. Variety 1 from the Cathedral of Regensburg is dominated by dolomite and displays high porosity created by late diagenetic dissolution of dolomite. The pore structure is characterized by intergranular pores and intracrystalline pores in the leached dolomite rhombohedra. On the other hand, the two varieties from the "Alte Pinakothek" in Munich are rich in calcite. As petrographic features indicate, this calcite was formed by incongruent dedolomitization during late diagenesis. The pore volumes of these two varieties are widely spreading. The amount of porosity developed depends on the type of the dedolomitization process, which, in turn, was strongly controlled by the pCO_2 of the pore solution. Low pCO_2 led to an calcite fabric due to incongruent dedolomitization. In the samples from the "Alte Pinakothek" this calcite precipitation effected a strong reduction of porosity.In the late stages of dedolomitization a rise in pCO_2 to values >0,5 atm induced a dissolution of the rest of the dolomite rhombs and peloids, leading to a rise in porosity and to the development of characteristic rhombohedral pores and dissolved particles.In the samples of the cathedral of Regensburg a high pCO_2 caused congruent dolomite dissolution and enhanced porosity formation.Thus, the partial pressure of CO_2 determined the formation of either a porous, dolomitic or a calcareous fabric during dedolomitization.The observed strong variations in the technical properties of the Grünsandstein are mainly due to the variations in the intensities of these two late diagenetic processes and due to their related changes in fabric and pore structure.

ZUSAMMENFASSUNG

Petrographische, geochemische und porenraumanalytische Untersuchungen des unverwitterten Regensburger Grünsandsteins vom Regensburger Dom und von der Alten Pinakothek, München ergaben 3 verschiedene Varietäten. Die Varietät vom Regensburger Dom ist durch Dolomit dominiert. Ihr hoher Porenraum entstand überwiegend durch eine spätdiagenetische Lösung von Dolomit. Es dominieren intergranulare Poren und interkristalline Poren in den angelösten Dolomiterhomboedern. Dagegen sind die Proben der zwei Varietäten von der Alten Pinakothek kalzitreich. Petrographische Kriterien belegen, daß der Kalzit in der späten Diagenese durch inkongruente Dedolomitisierung entstanden ist. Die Größe des Porenraum dieser Varietäten schwankt stark. Seine jeweilige Ausprägung ist sehr stark vom konkreten Verlauf dieses Dedolomitisierungsprozesses abhängig, der wiederum vom pCO_2 im Porenwasser kontrolliert wurde. Der bei niedrigem pCO_2 durch inkongruente Dedolomitisierung entstandene Kalzit verursachte einerseits eine starke Reduktion des Porenraums während eine spätere Erhöhung des pCO_2 auf >0,5 atm andererseits eine Herauslösung noch verbliebener Dolomitpartikel und -kristalle verursachte. Hierdurch wurde der Porenraum wieder erhöht und es entstanden die charakteristischen rhomboederförmigen und partikelförmige Poren. Die jeweilige Porosität der Proben hängt stark vom Verhältnis dieser beiden Prozesse ab. Die starken Schwankungen in den technischen Eigenschaften des Grünsandstein sind wesentlich auf die Variationen in der Intensität dieser spätdiagenetischen Prozesse zurückzuführen.

RESUME

Par l'analyse pétrographique, géochimique et analyse de structure de pore sur des carottes cylindriques non altérées par les intemperies et prélevées de la cathédrale de Regensburg et de l'"Alte Pinakothek" à Munich trois variétés de "Regensburger Grünsandtein" pouvaient être constatées. Sur la variété 1 de la cathedrale de Regensburg la dolomite prédomine et développe une grande porosité crée par la dissolution diagenetique du dolomite. La structure de pore est caractérisée par des pores intergranulaires et intracristalines dans les dolomites lessivés. D'autrepart les echantillons des deux variétés de l'"Alte Pinakothek" à Munich sont riches en calcite. Comme montrent les caractéristiques pétrographiques la formation de calcite est due à une dédolomitisation incongruente pendant la diagenèse. Les volumes des pores de ces deux variétés varient largement. La porosité developpée dépend du type de procédé de dédolomitisation fortement contrôllée par le pCO_2 de la solution de pore. Le calcite des echantillons de l'"Alte Pinakothek" dû à une dédolomitisation incongruente etait développé lors d'un pCO_2 bas eu causé une forte réduction de la porosité. Mais plus tarde, une augmentation du pCO_2 à >0,5 atm est responsable pour la dissolution des rhombes et particles de dolomite. Ainsi la porosité augmentait de nouveau et les pores caractéristiques sous forme de rhombes et paricles se développaient. Dans les echantillons de la cathédrale de Regensburg un pCO_2 élevé a causé une dissolution de dolomites congruents et déclenche donc une augmentation de la porosité. La porosité des echantillons dépend largement de la relation de la dédolomitisation congruente et incongruente. Les variations fortes constatées dans les propriétés techniques du "Regensburger Grünsandstein" sont principalement dues aux variations dans les intensités des ces deux procédés diagenetiques.

Keywords: Grünsandstein, petrography, diagenesis, dolomitization, dedolomitization, dissolution of dolomite, pore structure analysis, pore size distribution, Hg-porosimetry, specific surface area, BET-method, rhombohedral pores, geochemistry

1. Introduction

The Grünsandstein coming from the region around Regensburg has been used as a building stone for a long time, e.g. for many parts of the Cathedral of Regensburg, the Cathedrals of Eichstätt and Passau, the Neue Residenz as well the Alte and Neue Pinakothek in Munich.
Traditionally, the cathedral site office in Regensburg distinguishes 3 varieties of the "Regensburger Grünsandstein" [1] named after their regional major occurence "Abbacher", "Ihrlersteiner" and "Pfalzer Grünsandstein". The technical properties of the Grünsandstein - e.g. compressive strength and water-absorbing capacity - vary in wides ranges like its mineralogical composition [2]. It seems that the reasons for these significant differences have not been investigated yet.
Therefore this article is aiming to clearifying the genesis of the distinct varieties by the means of sedimentary-petrographical, geochemical, and pore structure analysis. Moreover, the aim is to document the control of the diagenetic processes on the pore structure, by which important

technical properties like the water-absorbing capacity are determined.

The "Zentrallabor des Bayerischen Landesamt für Denkmalpflege" provided 4 cores from the nothern facade of the Cathedral of Regensburg and 12 cores from the Alte Pinakothek in Munich. They were divided into four parts and samples were taken from the unweathered inner part for thin section analysis, x-ray-fluorescence, and pore structure analysis by Hg-porosimetry and nitrogen-adsorption.
Parallel samples from the same block were used by Sattler and Wendler [2] for investigations on the technical properties relevant for conservation.

2. Petrographical description of the distinct varieties

2.1. Methodics

The thin sections were analyzed by petrographical criteria and at least 500 points were counted for the determination of the modale composition. The staining of the carbonates with alizarine S and potassium-ferricyanide allowed the distinction of dolomite, calcite, and Fe-calcite. Their composition and grain size distribution recommend a classification to the above mentioned "Ihrlersteiner" variety.

2.2. Variety 1 of the Cathedral of Regensburg

The drilling cores RGD 758, 761, 780, and 782 from two blocks of the northern facade must be classified as glauconite bearing, dolomitic, fine- to medium-grained sandstones. The compositonal data are listed in Tab.1.
The quartz content is relatively high. The second most abundant mineral is dolomite occurring predominantely as euhedrale, zoned rhombohedra of 100-300 μm diameter. They often display a core either rich in inclusions or with a fine porosity core and a clear fringe poor in inclusions.

The two are separated by an instable, often leached zone (Fig. 1, Fig. 2). Sometimes peloids with small dolomite crystals are preserved as relicts.

Sample	quartz vol%	feldspar vol%	calcite vol%	dolomite vol%	Fe-OOH vol%	glauco. vol%	others vol%	pores vol%
RGD758	45.15	1.46	0	23.03	2.19	12.98	1.45	13.70
RGD761	48.0	1.26	0	20.63	0.48	13.47	1.47	14.10
RGD780	41.66	1.70	0	20.40	7.82	13.43	3.84	10.88
RGD782	44.09	1.41	0	20.31	6.30	11.33	2.83	13.70
APMI	24.62	3.66	42.93	5.16	1.16	7.32	0.32	14.80
APMII	25.71	1.35	37.93	5.71	1.80	10.22	0.75	16.54
APMIII	25.68	1.03	35.44	2.56	4.62	9.76	1.71	16.54
APMIV	31.00	2.00	30.33	4.50	3.67	11.83	0.83	18.00
APMV	26.83	0.67	49.33	4.50	0.16	9.16	0.64	8.83
APMVI	33.00	1.16	37.67	6.40	2.13	11.45	0.57	7.57
APM7.3	17.17	1.20	47.43	8.90	6.50	8.22	0.68	9.93
APM8.2	26.55	0.95	39.27	3.65	5.88	7.00	0.63	16.00
W2K1	40.87	1.30	28.38	4.12	7.54	8.72	0.82	8.24
W2K4	49.02	1.46	31.58	3.41	1.09	4.51	0.12	8.78
W3K5	50.71	1.43	20.19	3.81	1.74	6.67	0.63	10.01
W3K8	50.40	1.74	20.19	3.81	4.93	7.15	0.31	11.13

Table 1: Composition of the samples according to point count analysis of the thin sections.

The rounded glauconite pellets partly show fissures resembling shrinkage cracks, dark, fine-crystalline inclusions, and small dolomite inclusions. Several carbonate peloides contain glauconite (it is generated by displacement of carbonates), or the glauconite is replaced by dolomite, rarely changed to chalcedony and dissolved. The glauconite of RGD 780 and 782 are often impregnated by Fe-hydroxide.
According to the dolomite fabric dolomitization proceeded in two steps: Relatively early in diagenesis a dolomitization of the peloids and echinoidal fragments occurred causing a finely crystalline dolomite fabric. Later in diagenesis, a recrystallization and growth of dolomite crystals is indicated by the clear fringes of the dolomite rhombohedra. This dolomite generation caused a reduction of porosity. During late diagenesis, variety 1 was subjected

to a dissolution of dolomite, which resulted in an enhancement of porosity by creation of intracrystal and intercrystal pores (Fig. 1).
An instable non-stoichiometric, Fe-rich zone between the core of the rhombohedra and the clear fringe was preferentially dissolved. This dissolution was caused by pore solutions with high pCO_2 which were undersaturated for both dolomite and calcite.

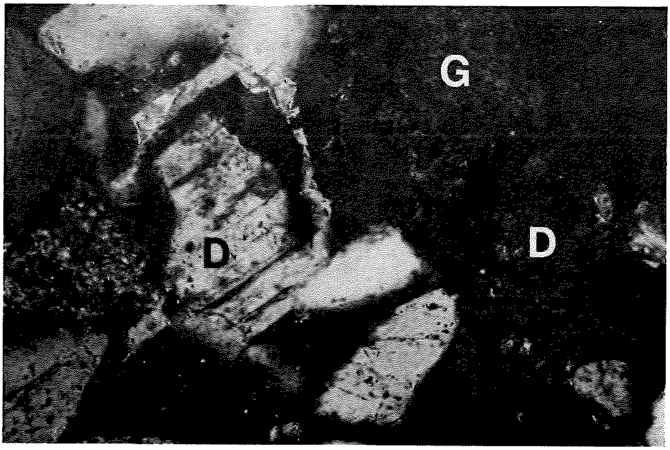

Fig.1: Dolomite rhombohedra (D) with dissolved zones and dissolutions along the cleavage cracks and at the inclusions in the core (quartz: light and dark grey, glauconite: G, pores dark). Variety 1, poor in Fe-hydroxides, RGD 758-3, thin section, crosspolarized light, magnification: small side of the picture ≈ 0.375mm.

During this dissolution phase, in the samples RGD 758 and 761 some Fe-hydroxide was precipitated in the intracrystal pores. But in the cores RGD 780 und 782 significantly more Fe-hydroxides wre precipitated, often filling the dissolved zones of the dolomite crystals, sitting in the intergranular pores, and impregnating glauconite so that the porosity is decreased by these abundant Fe-hydroxide cements (Fig.2).

The porosity measurable in the thin sections is relatively high (Tab.1). Intergranular pores dominate (Fig.1) over intracrystalline pores of the leached dolomite rhombohedra (Fig.2). Shrinkage cracks are sometimes formed around the glauconite grains.

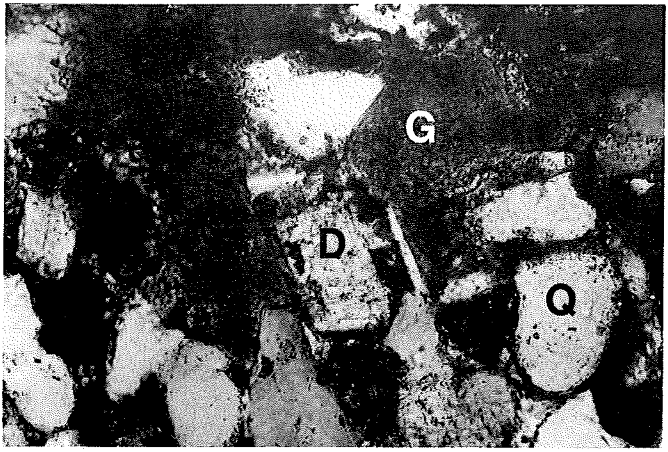

Fig.2: Fabric of the dolomitic variety 1 rich in Fe-hydroxides. Quartz light and dark grey (Q), dolomite (D) with brown Fe-hydroxide precipitated in the dissolved zone, glauconite (G) in greenish colours, pores dark. RGD 758-3, thin section, plane polarized light, magnification: small side of the picture ≈ 1.5mm.

2.3. Variety 2 from the "Alte Pinakothek"

These stones are classified as glauconite bearing, calcareous sandstones upto sandy lime stones. Tab.1 shows their modale composition.
The quartz content is low but spreads widely. The glauconite content lies on an average under the one of variety 1,

too. An indistinct bedding of quartz rich and carbonate rich layers is developed. This variety shows an higher content of biogenic particles than variety 1.

The carbonate phase consists of Fe-zoned sparry calcite (Fig.3). The distribution of calcite varies strongly between the sedimentary beds. Layers rich in quartz with some spots of sparry calcites and high intergranular porosity occur next to layers with a dense calcite-mosaic texture between the quartz grains. In these relatively dense fabrics the pores in the size of grains are the dominating type of pores. Some pores show a rhombohedral contour (Fig.5).

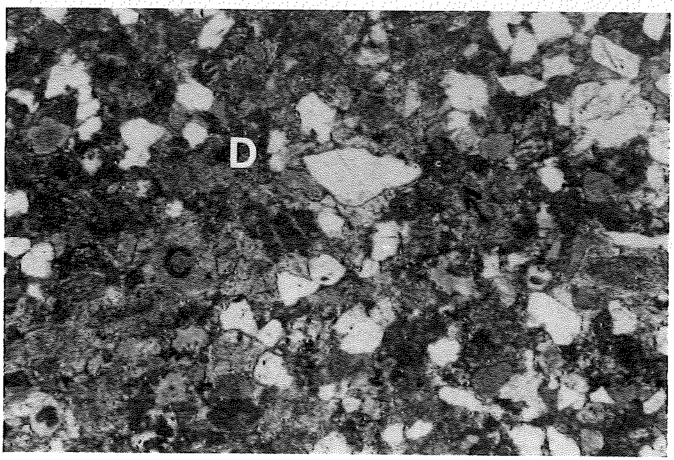

Fig.3: Fabric of the calcareous variety 2 of the "Alte Pinakothek" with large, partly zoned sparry calcites (C). The crystals surround relics of dolomitic peloids and various foraminifers species. Dolomite (D) is fine-crystalline; in places, the dolomitic particles are strongly etched. APM 7.3-3, thin section, plane polarized light, magnif.: small side of the picture ≈ 1.5mm.

In the calcite rich areas there are sometimes Fe-hydroxides to be seen tracing the shape of rhombohedra (Fig.4). In some samples Fe-hydroxide covers the walls of pores, but can also be enriched in forms of rinds. Rhombohedral pores are the most important pore type beside the pores from dissolved particles.

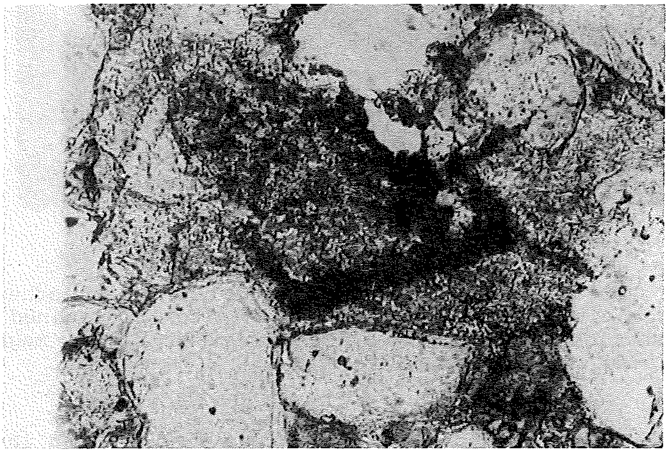

Fig.4: A rhombohedral fringe of Fe-hydroxide surrounds a area of calcite rich in inclusions and traces a former dolomite rhombohedron. APM VI-3, thin section, plane polarized light, magnif.: small side of the picture ≈ 0.3mm.

2.4. Variety 3 of the "Alte Pinakothek"

This samples can be classified as a glauconite bearing, and calcareous coarse sandstone showing strong variations and rich in biogenes (Tab.1).

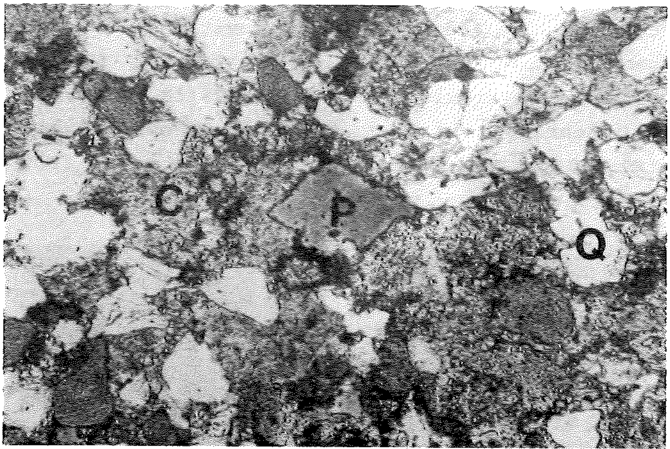

Fig.5: Pore (P) with rhombohedral outline in an otherwise dense calcite fabric. Quartz (Q), calcite (C) stained red, thin section, APM 8.2-3, plane polarized light, magnif.: small side of the picture ≈ 990 μm.

There are coarse sandy beds as well as fine-grained layers, calcite rich areas, and even biopelmicrite lenticular layers (Fig.6). The quartz content is high, but varying. Sporadically large, slightly dissolved feldspars may occur. In several samples an alternating bedding of coarse-grained, quartz rich and fine-grained, calcite rich layers could be observed. The calcite fabrics are - similar to those of variety 2 - dominated by zoned sparry calcites. Dolomite is to be found only in a few, still existing peloids.As the relict of dolomite peloids and dolomite rhombohedra indicate, both varieties of the "Alte Pinakothek" were dolomitized relatively early in diagenesis. Constrasting to variety 1, an incongruent dedolomitization occured during late diagenesis leading to dissolution of dolomite and precipitation of calcite.

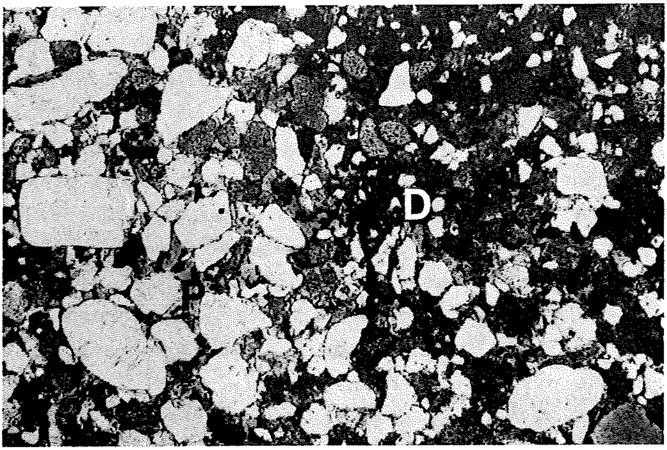

Fig.6: Fabric of variety 3 with an interbedding of a coarse, bimodale, and quartz rich layer and a fine-grained, carbonate rich layer. The fine-grained, carbonate rich layer contains some dolomite relics (D) and is denser than the quartz rich layer where the intergranular pores (P) dominate. W2K1-1, thin section, plane polarized light, magnif.: small side of the picture ≈ 3mm.

This incongruent dedolomitization is indicated by the presence of rhombohedral seams of Fe-hydroxides in the calcite mosaic (pseudomorphs after dolomite), by relictic dolomite in some peloids and in glauconite pellets indicating the presence of former dolomite. Rhombohedral pores point to the dissolution of dolomite rhombohedra. The incongruent dedolomitization process proceeded in pore solution with low pCO_2 (<0,5 atm), low Mg/Ca ratio , and in an open system which allowed the removal of dissolved Mg [3] and the importation of Ca. The Fe rich zones of the calcite crystals suggest that the pore solutions were initially slighty reducing. But during the course of dedolomitization a change to oxidizing conditions induced the formation of Fe-hydroxides.

Incongruent dedolomitization lead to a strong reduction of visible porosity in thin section. Later, the composition of the solution changed. pCO_2 rose to values above 0.5 atm, the pore solutions became undersaturated for dolomite and (slightly) for calcite too. These changes caused the dissolution of dolomite peloids and the dissolution of dolomite rhombohedra leading to the formation of rhombohedral pores. Thus, porosity was increased again. The extent of this final porosity enhancement depended of the relative intensities of incongruent dedolomitization to congruent dolomite dissolution which depended mainly of the changes of the pCO_2 in the pore solution.

3. Pore structure analysis

3.1. Methodics

By means of mercury (Hg)-porosimetry the porosity and the pore size distribution, respectively, can be measured over a pore radius range from 60 μm to 4 nm. The specific surface area and the pore size distribution for pores with radii smaller than 30 nm was calculated from N_2-adsorption isothermes applying the BET- and BJH-method. The pores are classified according to their radius in coarse pores (6-60μm), macropores (6μm-40nm), mesopores (40-4nm), and micropores (<1nm). Pores with a radius >60μm could not be measured technically, unless those pores had smaller necks.

The results of the pore structure analysis are to be interpreted on the basis of the before described thin section petrography.

3.2. The pore space of variety 1 of the Cathedral of Regensburg

The two types of variety 1 determined by the thin section analysis are also indicated by different porosities. The porosity of type 2 (RGD 780 and 782) lies with 20.9 vol% and 21.0 vol% significantly under the porosity of type 1 (RGD 758 and 761) having 23.4 vol% and 24.4 vol% (Tab.2, Fig.7). The porosity is dominated by the coarse pore volume.

Samples	porosity (vol%)	intrusion volume (mm3/g)	BET-spec. surface area (m2/g)
RGD758	22.53-24.37	110.38-119.5	10.54
RGD761	23.6-25.17	116.57-123.59	10.46
RGD780	20.3-21.51	94.62-100.47	9.63
RGD782	20.95-21.07	95.77-97.91	9.93
APMI	23.14	104.63-111.95	8.84
APMII	15.71-17.7	68.22-77.35	7.07
APMIII	21.82-22.05	105.43-105.79	8.29
APMIV	23.41-24.55	111.54-118.71	8.68
APMV	17.35-19.5	79.11-90.56	6.87
APMVI	7.51-8.14	30.06-33.11	5.43
APM7.3	17.75-20.73	77.4-96.73	8.25
APM8.2	18.2-18.55	82.59-83.89	5.93
W2K1	17.34-22.18	89.06-114.6	9.10
W2K4	9.37-11.01	39.06-49.83	5.35
W3K5	10.18-11.13	42.93-45.47	2.59
W3K8	11.47-11.49	47.46-48.51	6.06

Table 2: Porosity, mercury intrusion volume, and BET specific surface area of the 3 varieties of the "Regensburger Grünsandstein".

The relative pore size distributions of RGD 758 and 761 show a plateau-like shape for the pore classes of 6-8μm, 8-10μm and 10-20 μm or (Fig.8). The maximum in the pore class 10-20μm reflects the intergranular pores in the thin section with diameters between 20 and 50μm.The pores with smaller radii are related to a variable extent to the in-

tracrystalline pores of dolomite and the cracks in and around the glauconite grains.
The relative pore size distributions of RGD 780 and 782 deviate widely from those of type 1. The relative pore volume of class 10-20μm is visibly smaller. Both the ratio of coarse pores and the lower porosity may reflect the cementation of the intergranular pores by Fe-hydroxide.
In contrast to the samples RGD 758 and 761 the mesopore volume of type 2 is remarkable higher which may be assumed to be another result of the higher contents of fine-crystalline Fe-hydroxides (Fig.7).

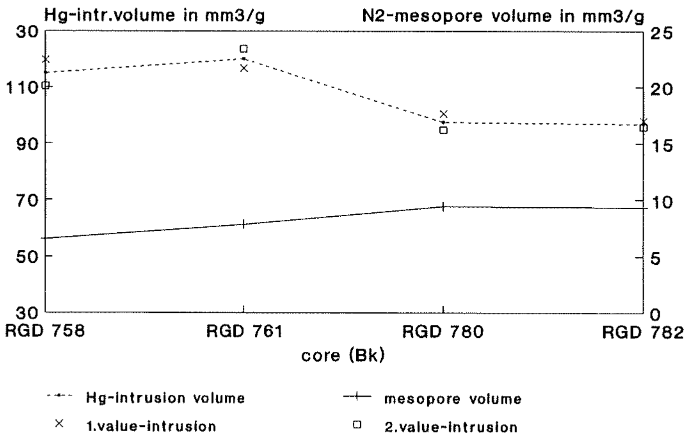

Fig.7: Comparison of the pore volume of the Hg-porosimetry and the N_2-sorption for the dolomitic variety 1 of the Cathedral of Regensburg

The specific surface area is high on an average of 10.14 m^2/g correlating with the meso- and micropores <4nm (Fig.9).

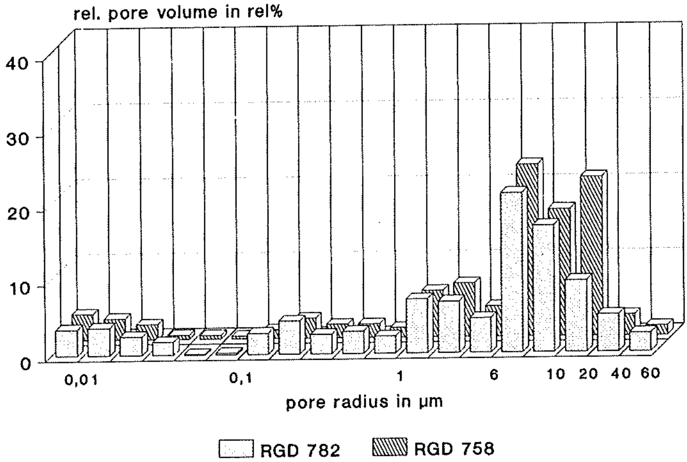

Fig.8: Relative pore size distributions in pore classes of the Fe-hydroxide rich sample RGD 758 and Fe-hydroxide poor sample RGD 782.

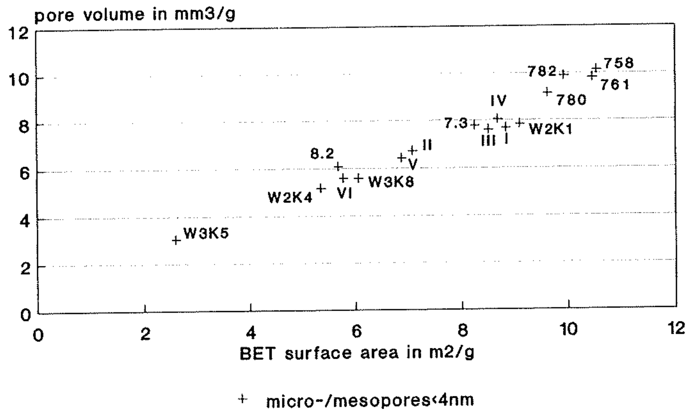

Fig.9: Correlation of the micro-/mesopore volume calculated from the N_2-desorption branch and the BET specific surface area of the 3 varieties of the "Regensburger Grünsandstein".

3.3. The pore space of variety 2 of the "Alte Pinakothek"

Following the thin section analysis two types may be distinguished as end members on a profile of certain properties. Hence, the samples APM V and APM 7.3 have low porosity in the case of a high calcite content (Fig.10), low quartz content (Fig.11) and low glauconite content. In comparison, the samples APM III and APM IV, slightly richer in quartz and poorer in calcite, are significantly more porous and have a higher content of glauconite. APM VI being very dense has a mean content of calcite.

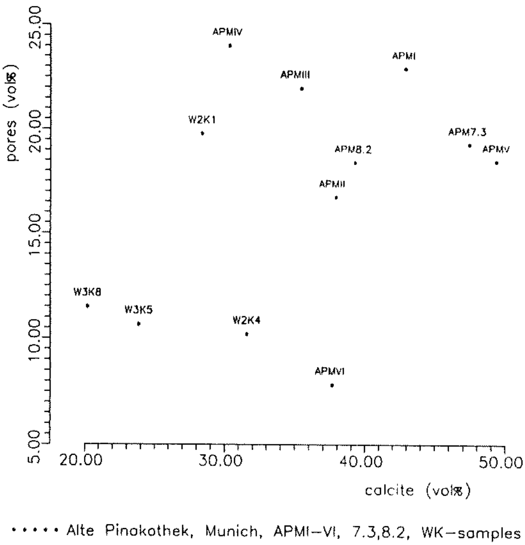

Fig.10: Correlation of the calcite content and pore space from thin section analysis of the calcareous samples of the "Alte Pinakothek". Two clusters of differing porosity are formed showing a negative correlation.

The porosities of the calcareous APM-samples - on an average of 18.97 vol% (Tab.2) - are lower than those of the dolomitic variety 1 and are also controlled by the coarse pores (Fig.12).

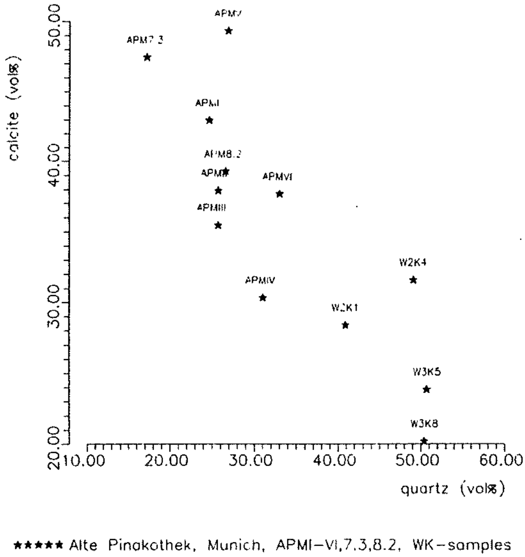

Fig.11: Correlation of the quartz and calcite content from thin section analysis of both varieties of the "Alte Pinakothek" showing a negative correlation.

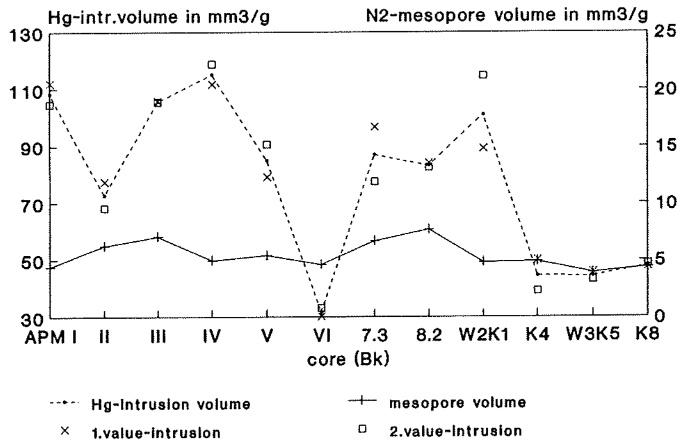

Fig.12: Comparison of the pore volume of the Hg-porosimetry and the N_2-sorption for the calcite dominated varieties 2 and 3 of the "Alte Pinakothek".

The calcite rich layers appear fairly dense in the thin sections but contain partly or totally dissolved particles (dolomite rhombs, peloides or glauconite) which, having a diameter of 100-300μm, cannot be detected by Hg-porosimetry. The occuring rhombohedral pores result from dissolved dolomite rhombohedra. In the more porous, calcite poorer layers intergranular pores dominate.

The end members determined by thin section analysis are found in the pore structure analysis: APM IV has the highest porosity with 23.98 vol% and the lowest calcite content. In contrast, APM V and 7.3 have lower porosities of 18.4 and 19.2 vol% connected with a higher calcite content. The sample APM VI differs from the other cores because of its very low porosity of 7.8 vol%. According to the sampling of a dense calcareous layer or a porous quartz rich layer the porosity may also vary in a single core.

Compared to the results from variety 1 another pattern can be seen in the pore size distributions of the calcareous samples (Fig.13). Especially the porous samples (APM III, IV) possess a large maximum in the pore class 10-20μm. The intergranular pores of the calcite poor areas observed in the thin section may fall to some extent into this class. This maximum stands in contrast to the observation of dissolved peloides and rhombohedral pores in a pore size with a radius >60 μm in thin section . It is likely that part of these pores are gathered in the pore class 10-20μm, when they are associated with small necks. The less porous APM VI does not show such a maximum. Some dolomite peloides (and some glauconite grains) are only partly dissolved. Thereby a high intercrystalline porosity is created which may be belong to the pore class <10 μm.

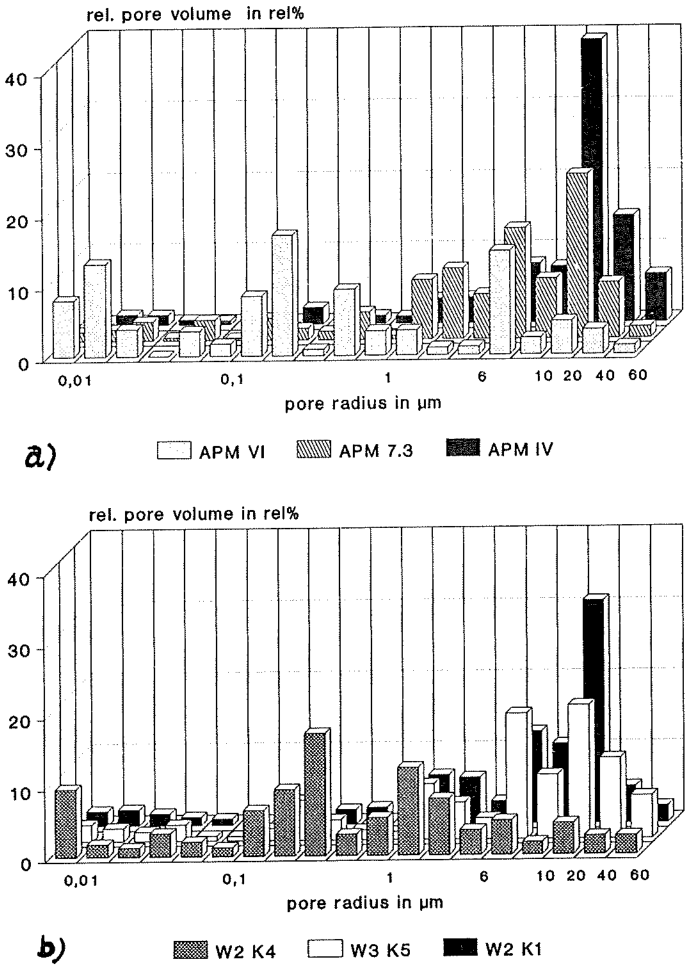

Fig.13: Relative pore size distributions in pore classes of a) the calcareous samples APM IV, 7.3 and VI of the "Alte Pinakothek" and b) the coarse-grained calcareous samples W2K1, W2K4 and W3K5.

The volume of mesopores (r<30nm) is positively correlated with the amount of fine-crystalline Fe-hydroxide. The volume of meso-/micropores is related to the specific surface area (Fig.9), which itself correlates to the Al_2O_3-content (Fig.14). The two correlations allow to draw the conclusion that the content of clay minerals (glauconite) is a major factor for the microporosity and specific sur-

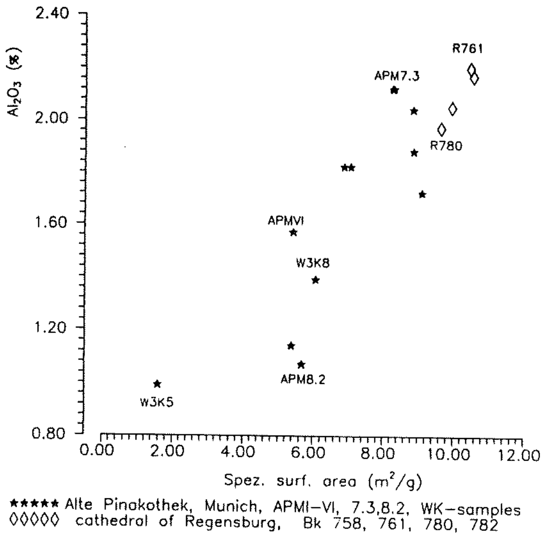

Fig.14: Correlation of Al_2O_3 content and BET specific surface area of the 3 varieties of the "Regensburger Grünsandstein".

3.4. Variety 3 of the "Alte Pinakothek"

The samples WK rich in quartz predominantly possess relatively low porosities (10.2 - 11.5 vol%), except W2K1 lying with 18.9 vol% in the range of the APM-samples (Tab.2, Fig.12). The pore structure depends on the type of fabric described in 3.3. In the calcite richer layers particle-molds dominate which may have rhombohedrally formed edges. Dissolved discrete dolomite rhombohedra occur less frequently. The low porosities of W2K4 and W3K8 probably reflect the sampling of areas richer in calcite.
In contrast to the other varieties, the total intrusion volume is not clearly controlled by the coarse pores, since

the variations of the coarse pore volume is compensated by variations of the mesopore volume.

As for the varieties 1 and 2, the volume of pores with radii <4nm is correlated to the specific surface area and the Al_2O_3-content (Fig.9 and 14).

4. Geochemistry

4.1. Methodics

Fused tablets of the unweathered inner cores were investigated by fluorescent x-ray analysis for the major and subordinate elements. For determination of Fe-content the amount of Fe^{2+} and Fe^{3+} is given as total Fe-content in the trivalent form. The correlations of the major elements are amplified by use of mass percentage (m%). In the case of the variety 1 the 4 cores were sampled twice and labeled with a and b, respectively.

4.2. Geochemistry of variety 1

The geochemical analysis also reflects the two types of variety 1. They differ as well in the content of CaO and MgO (dolomite) as in the content of SiO_2 (predominantly quartz) and Al_2O_3 (mainly glauconite).

CaO and SiO_2 show a negative, but strongly scattering correlation to each other reflecting the initial quartz/carbonate ration as well as its alterations by diagenetic carbonate dissolution and processes of cementation (Fig.15).

Since dolomite is the only carbonate phase present, MgO and CaO are well correlated (Fig. 16).

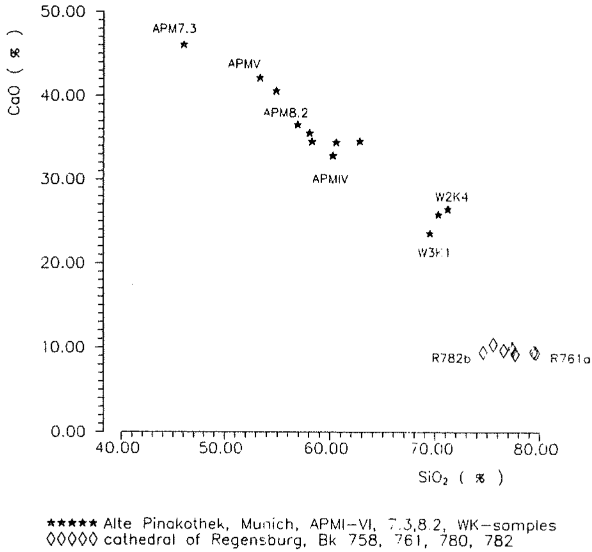

Fig.15: Correlation of SiO_2 and CaO content of all 3 varieties showing a negative correlation factor and a wide spreading. The varieties form clusters.

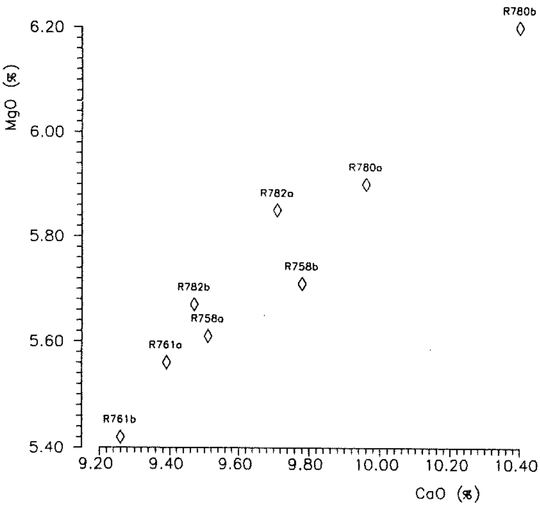

Fig.16: Correlation of MgO and CaO content of the dolomitic samples of the Cathedral of Regensburg.

A positive correlation exists between Fe_2O_3 and MgO at low Fe_2O_3-contents (Fig. 17) indicating that dolomite is a main source of the Fe-content. Enrichment of Fe_2O_3 by precipitation of Fe-hydroxides superpose this relation at higher Fe_2O_3 contents.

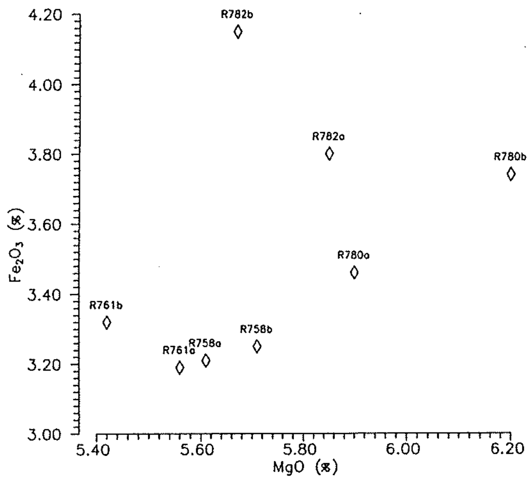

Fig.17: Correlation of MgO and Fe_2O_3 content of the dolomitic samples of the Cathedral of Regensburg. The two types show clearly distinct clusters.

An indistinct negative correlation seems to be developped between Fe_2O_3 and Al_2O_3 (Fig. 18). This correlation might be controlled by the influence of high Fe-hydroxide content in the cores 780 and 782 which is accompanied by higher dolomite content and lower quartz and glauconite contents compared with the cores 758 and 761.

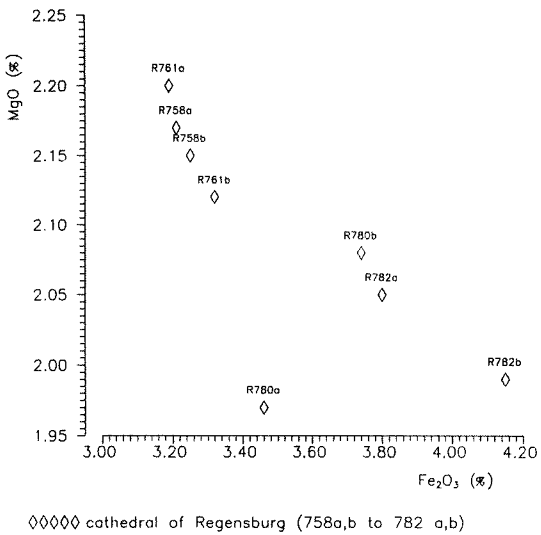

Fig.18: Correlation of Al_2O_3 and Fe_2O_3 content of the dolomitic samples of the Cathedral of Regensburg. The two types show clearly distinct clusters.

4.3. Geochemistry of the varieties 2 and 3

These samples are characterized by their predomination of calcite and their geochemical composition and therefore differ strongly from the composition of variety 1 especially due to the lacking correlation between CaO and MgO (Fig.19).

The clusters in the correlation of SiO_2 and CaO reflect the petrographic differences of variety 2 and 3 and are controlled by the relation between diagenetic calcite to the initial quartz content (Fig.19).

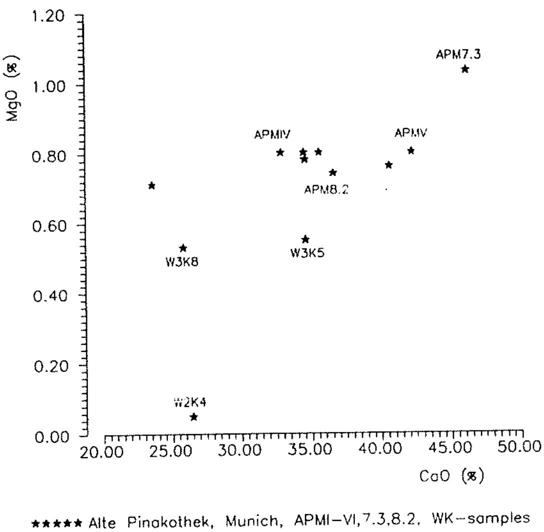

Fig.19: Correlation of MgO and CaO content of the two calcareous samples of the "Alte Pinakothek".

The low MgO content and the Fe_2O_3 content are both correlated with Al_2O_3 indicating that the content of both oxides is rather controlled by glauconite than by the low dolomite content. But the occuring dolomite relics and the Fe-hydroxides result in a scattering auf the MgO and Fe_2O_3 correlations.

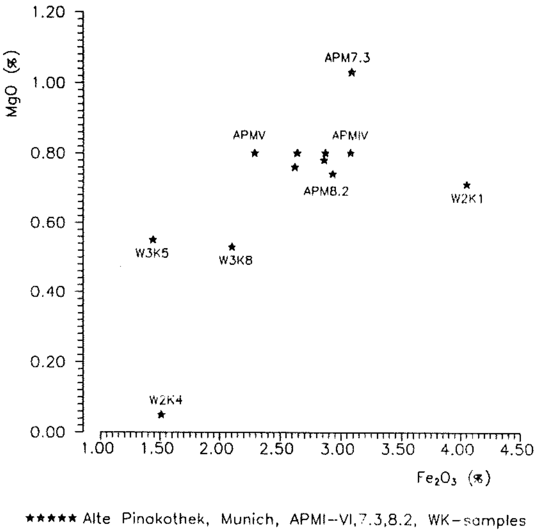

Fig.20: Correlation of MgO and Fe_2O_3 content of the two calcareous varieties of the "Alte Pinakothek" correlating only slightly and spreading widely.

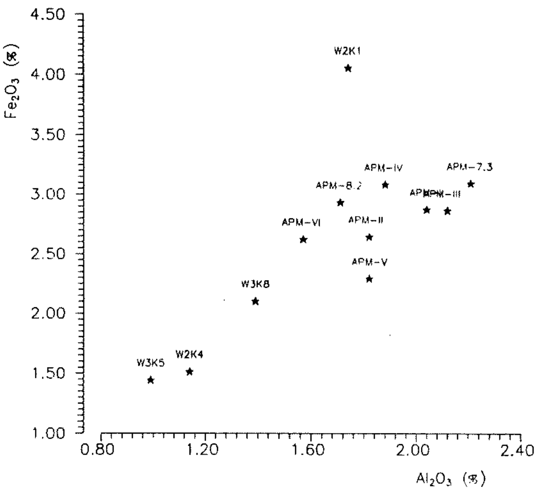

Fig.21: Correlation of Al_2O_3 and Fe_2O_3 content of the two calcareous varieties of the "Alte Pinakothek" showing the predominating influence of glauconite on the Fe_2O_3 content.

5. Conclusions

The formation of distinct varieties of the Grünsandstein is a result of both the actual conditions of sedimentation and diagenetic processes proceeding after sedimentation. Especially those processes concerning the carbonates had a great influence on the fabrics of the "Regensburger Grünsandstein" like the dolomitization and above all the late diagenetic, congruent and incogruent dedolomitization. This process changed the petrographical structure, the geochemical composition as well as the pore structure tremendously. The particular amount of the pore volume is depending on the specific course of the dedolomitization which in turn was controlled by the pCO_2 of the pore solution. Low pCO_2 induced calcite formation by incongruent dedolomitization and thus gave rise to a strong reduction of porosity. Later, an increase of pCO_2 to >0.5atm caused congruent dissolution of most of the remaining dolomite rhombs and particles. This late dolomite dissolution increased the pore space again and led to the formation of the particle-mold and the characteristic rhombohedral pores. The height of the redox-potential and its changes during the dedolomitization controlled the formation of Fe-hydroxide decreasing the porosity by cementation inside the pores.
Thus, the formation of distinct varieties of the "Regensburger Grünsandstein" is in great parts only a result of variing intensities of a few processes during diagenesis.

6. Literature

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