

The Permian-Triassic Boundary in the Carnic Alps of Austria (Gartnerkofel Region)			Editors: W.T. Holser & H.P. Schönlaub	
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The Permian-Triassic of the Gartnerkofel-1 Core (Carnic Alps, Austria): Strontium Isotopes and Carbonate Chemistry

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With 7 Text-Figures and 3 Tables

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*Carinthia
Carnic Alps
Permian/Triassic Boundary
Carbonate Rocks
Strontium Isotopes*

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Zusammenfassung

Aus verschiedenen Abschnitten des 330 m langen Bohrkerns der Forschungsbohrung Gartnerkofel-1 wurden 27 Proben von möglichst reinen Karbonatgesteinen ausgewählt (Tabelle 1), die Karbonatzusammensetzung röntgenographisch analysiert und im Zusammenhang mit Haupt- und Spurenelementgehalten (P. KLEIN, in diesem Band) interpretiert. Der überwiegende Teil der Proben besteht vermutlich aus primärem Ca-Dolomit mit geringer Beteiligung von Mg- Calcit. Nach den Spurenelement-Daten wurden sie in unterschiedlichem Ausmaß von einer spätdiagenetischen Rekristallisation betroffen.

Aufgrund von 12 bestimmten $^{87}\text{Sr}/^{86}\text{Sr}$ -Verhältnissen wird angenommen, daß die Schichtfolge an der Perm/Trias-Grenze größtenteils aus fröhdigenetisch gebildeten Dolomiten besteht, die aber unterschiedlich rekristallisiert sind. Die Aufnahme des radiogenen ^{87}Sr in die Karbonate erfolgte entweder durch diagenetische Dolomitrekristallisation teils in Kontakt mit meteorischen Wässern (in den Proben 111 [184,72 m] und 198 [226,12 m]), teils durch zirkulierende Lösungen durch die Karbonatplattform.

Abstract

Twenty seven fairly pure carbonate samples across the Gartnerkofel core-1 were analyzed by x-ray diffraction and 1N-HCl leachable main and trace element composition (P. KLEIN, this volume) were interpreted. The bulk of the investigated samples are most likely primary Ca-dolomite with small amounts of Mg-calcite. Trace element chemistry indicates variable degrees of later diagenetic recrystallization.

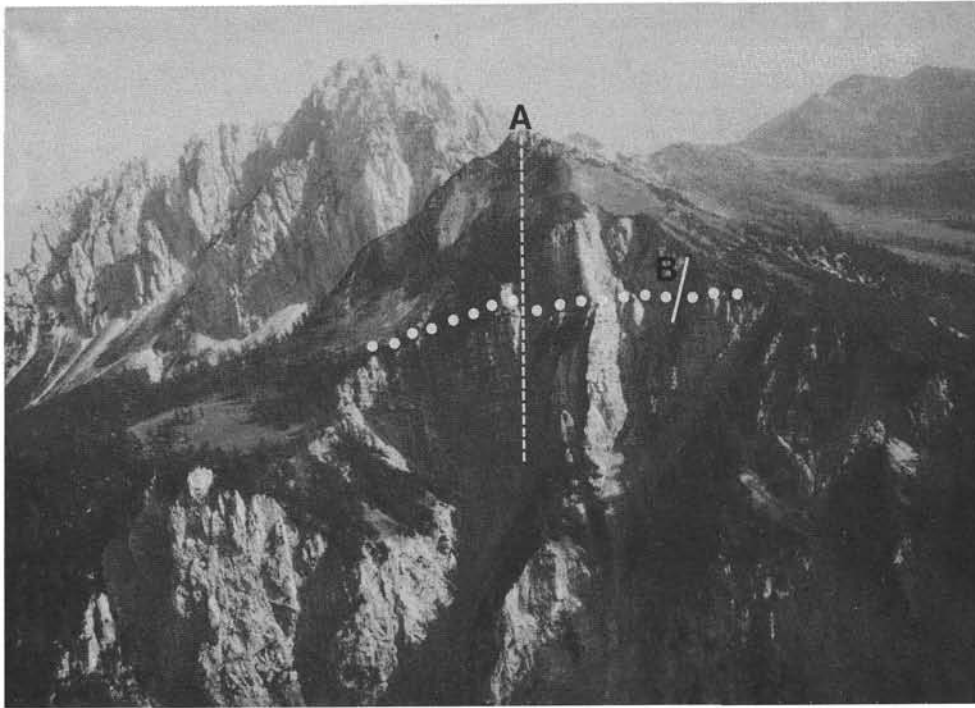
Twelve $^{87}\text{Sr}/^{86}\text{Sr}$ ratio measurements support the variable degree of diagenetic dolomite recrystallization (radiogenic ^{87}Sr * uptake) most likely by meteoric water brines in particular in the samples 111 (184.72 m) and 198 (226.12 m) or circulating fluids through the carbonate platform.

1. Introduction

The isotopic composition of strontium in carbonate rocks has become an important diagnostic tool for diagenetic and paleoceanographic studies. The application of Sr isotopes to understand carbonate dia-

genesis has been fostered by the analysis of natural fluids such as modern seawater, river water, and subsurface brines for Sr isotopes and the construction and refinement of a "seawater curve" of $^{87}\text{Sr}/^{86}\text{Sr}$ through time, based on analyses of marine carbonates of known age.

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Text-Fig. 1.
Aerial photograph from the north of the Reppwand with the Gartnerkofel (2195 m) in the background. A: Drill site on Kammleiten (1998 m); B: Top of the outcrop section. Dotted line indicates the Permian-Triassic boundary between the Bellerophon Formation (below) and the Werfen Formation above. Photo: G. FLAJS, Aachen.

"Age curves", displaying variations of isotope ratios with time, have been one of the most fruitful approaches to the study of seawater paleochemistry. No definitive study has yet been made of the secular variation of marine strontium isotopes in the P-Tr interval. W.T. HOLSER and M. MAGARITZ (1987) however, have summarized the values in the literature. $^{87}\text{Sr}/^{86}\text{Sr}$ ratios reach a low at the uppermost Permian which is approximately matched only by Upper Jurassic (W.H. BURKE et al., 1982) carbonates.

Diagenetic carbonates can have Sr isotopic compositions that deviate from the marine value, and these variations can be ascribed to either various nonmarine diagenetic processes, or to diagenesis by younger seawater of different isotopic composition. These approaches have been particularly useful towards addressing some fundamental questions regarding dolomitization.

In addition x-ray diffraction data of the carbonate phase (H. FÜCHTBAUER & H. GOLDSCHMIDT, 1965) and main as well as trace element chemistry of carbonate rocks (P. KLEIN, this volume) are good indicators of the diagenetic evolution of carbonate rocks (J. VEIZER, 1983).

From the carbonate samples of the Gartnerkofel drill core-1 ten fine grained and two coarse grained samples (No. 38, 171) have been selected in order to evaluate the possibility of establishing the marine $^{87}\text{Sr}/^{86}\text{Sr}$ changes at the Permian/Triassic boundary and to trace diagenetic changes due to recrystallization or tectonic activity. In order to confirm trends established by Sr-isotopic ratios 17 additional fairly pure carbonate samples have been included in the trace element evaluation of the diagenetic dolomitization.

2. Analytical Techniques

Unoriented carbonate powder patterns were measured by x-ray diffractometry. The range of 24–37 degrees ($\text{Cu K}\alpha_{1,2}$) have been scanned $1/4^\circ/\text{min}$ and cor-

rected to the quartz reflection $[(101) 26.66^\circ 2\theta]$. Standard deviation of repeated measurements was $\pm 0.02^\circ 2\theta$.

About 120 mg carbonate powder was dissolved using cation-exchange resin. The measurements of the Rb and Sr isotopes were performed with a special mixed spike (high Sr, low Rb) as described by M. KRÁLIK (1984). Several samples were measured twice unspiked and spiked. The Rb corrected $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in Table 1 (Text-Fig. 5) take into account the radiogenic $^{87}\text{Sr}^*$ added due to the isotopic decay of small amounts of Rb present in the carbonate phases since deposition 245 Ma ago (see Text-Fig. 3a). The weighted means of 15 independent measurements (five during this study) of the standard SRM 987 is $^{87}\text{Sr}/^{86}\text{Sr} = 0.70995 \pm 6$. All values reported here are corrected to a SRM 987 $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of 0.71014.

3. X-ray Investigations

The results of the carbonate phase composition and the peak position of the strongest (104) reflection are presented in Tab. 1 and in Text-Fig. 2. They indicate three main carbonate parageneses, most including two phases:

- 1) Samples dominated by stoichiometric calcite with Ca-dolomite (approx. 5 mol-% Ca; sample No. 184, 35 and 38).
- 2) The bulk of the investigated dolomite samples are Ca-dolomite (1–2 mol-% Ca) with 0–3 % of Mg-calcite.
- 3) Ca-dolomite (2–3 mol-% Ca) with small amounts of Mg-calcite (approx. 20 mol-%; samples No. 111 and 171).

Ca-dolomites are characteristic for primary dolomites. The different carbonate parageneses indicate, however, a more complicated diagenesis with various stages of recrystallizations in time.

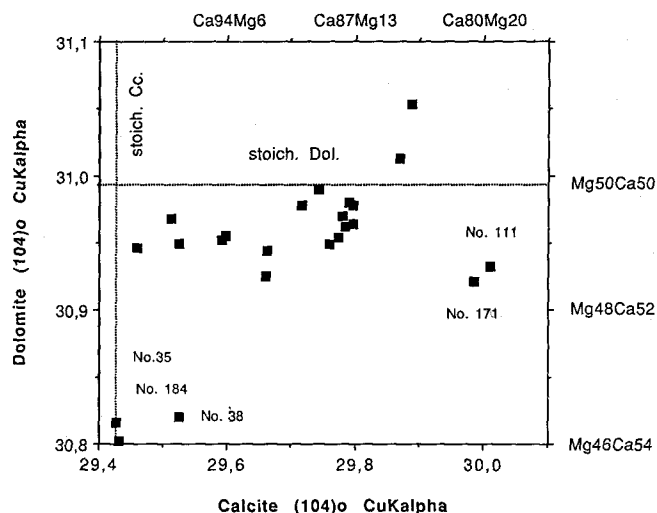
Table 1.
XRD-data of Gartnerkofel drill core-1 carbonates.
Dolomite, Calcite (104) peak position in degree 2 θ . Small amounts of plagioclase are present in samples No. 26, 198, 200 and 201. In sample No. 35 are indications for fluorite(?).

Sample No.	Depth [m]	Dolomite [%]	Calcite [%]	Quartz [%]	Dolomite (104)	Calcite (104)
20	82.90	94.0	2.1	2.0	30.980	29.790
26	90.60	70.0	15.0	13.0	30.954	29.773
35	102.90	55.0	43.0	2.0	30.816	29.426
38	105.30	73.0	0.8	5.0	30.820	29.525
57	130.40	94.1	4.5	1.4	30.964	29.796
79	158.30	98.5	1.0	0.5	30.968	29.512
111	184.72	92	5.0	1.0	30.932	30.011
126	187.10	90.0	6.0	2.0	30.925	29.659
153	195.20	95.0	0.1	3.0	30.962	
165	202.00	98.0	1.0	0.5	30.942	
171	207.10	97.0	1.0	0.5	30.921	29.986
184	215.70	3.0	90.0	2.0	30.802	29.432
198	226.12	97.5	2.0	0.5	30.952	29.591
200	228.94	99.0	0.5	0.5	31.053	29.888
201	229.12	99.0	0.5	0.5	31.013	29.869
204	229.92	93.0	0.5	3.0	30.978	
204C	229.90	96.0	0.5	3.0	30.978	29.716
206	231.25	97.0	0.5	0.5	30.890	
207	231.57	95.0	0.5	0.5	30.955	29.597
208	231.72	95.0	0.5	1.0	30.946	29.459
209	233.06	96.0	0.5	0.5	30.995	
215	237.84	97.0	0.5	0.5	30.928	
223	251.00	95.0	1.0	0.5	30.949	29.524
247	277.98	99.5	0.5	0.0	30.944	29.662
257	289.10	98.0	0.5	0.0	30.990	29.742
269	297.80	97.0	3.0	0.0	30.978	29.797
270	298.10	97.0	3.0	0.0	30.970	29.781
281	312.10	96.0	3.0	0.0	30.962	29.785
301	330.00	96.0	4.0	0.0	30.949	29.759

4. Trace Elements of Bulk Carbonate Samples

The mean values and the range of trace elements leachable from carbonate rocks by gentle HCl (P. KLEIN, this volume) are summarized in Tab. 2 and shown in Text-Fig. 3. The elements Co, Cr, Fe, Mn, P, S and Ti correlate with the acid insoluble residue, and the leached Al and K content. An attempt was made to correct these element concentrations assuming the intercept at zero percent insoluble residue. (Al, K) are the true mean concentrations in the carbonate phase with no addition from the silicates.

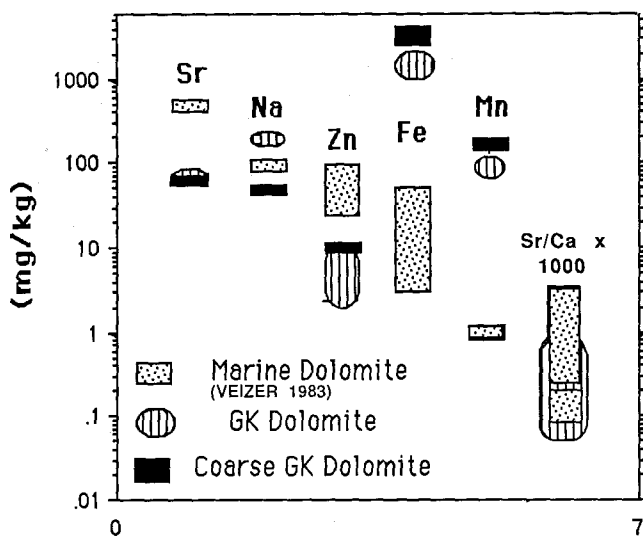
Iron, manganese are considerably higher, whereas sodium is slightly higher in Gartnerkofel dolomite rocks than dolomite in equilibrium with modern sea water (J. VEIZER, 1983). Coarse-grained Gartnerkofel dolomite



Text-Fig. 2.
Position of the calcite (104) peak versus dolomite (104) peak indicate three carbonate parageneses:
1) Ca-dolomite (1-2 mol.-%) with small amounts of Mg-calcite (2-12 mol.-%).
2) Mainly stoichiometric calcite with Ca-dolomite (5 mol.-%, No. 35, 38, 184).
3) Ca-dolomite (2-3 mol.-%) with small amounts of Mg-calcite (20 mol.-%, No. 111, 171).

(sample No. 38 and 171) is even more enriched in Fe and Mn. Na however is depleted compared to marine „equilibrium” dolomite. The elements Sr and Zn in the Gartnerkofel dolomites are depleted compared to marine “equilibrium” dolomite (Text-Fig. 3). The Sr/Ca \times 1000 ratio of the Gartnerkofel dolomites ranges from values obtained from primary dolomites to the full range of secondary dolomites (J. VEIZER & R. DEMOVIC, 1974).

These controversial data seems to indicate that from clearly primary dolomite, especially in the Bellerophon horizon (highest mean Na, $\delta^{13}C$, $\delta^{18}O$ and lowest Mn values, [K. STATTEGGER, this volume]), carbonates or parts of it have recrystallized partly or wholly during diagenetic evolution. The relatively high Na content



Text-Fig. 3.
Trace element composition of marine dolomite (J. VEIZER, 1983) in comparison to fine and coarse grained dolomite of the Gartnerkofel drill core-1. The upper column of the Sr/Ca ratios represents early diagenetic dolomite. The lower column represents late diagenetic dolomite.

Table 2.

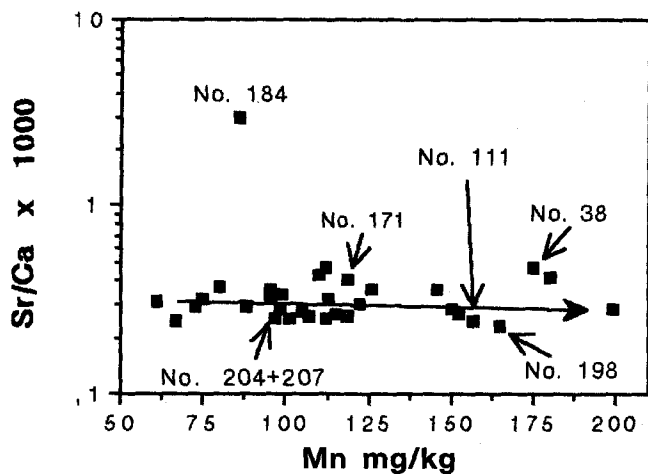
Mean values and Standard Deviation of main mineral phases of 27 selected relatively pure carbonate samples across the Gartnerkofel core. Mean values of the chemical elements and isotopes are from the same samples (see KLEIN and MAGARITZ and HOLSER this volume). Some element contents were corrected for residues or K-content.

Mineral, Element	Mean (± 1 SD)	Mean corr.	Elements	Mean (± 1 SD)	Mean corr.
Dolomite [%]	94.5 \pm 5.3		Ni [mg/kg]	1.4 \pm 0.9	
Calcite [%]	1.9 \pm 3.2		S [mg/kg]	309 \pm 973	
Quartz [%]	1.6 \pm 2.7		Sr [mg/kg]	68 \pm 14	
Residue [%]	4.4 \pm 5.4		P [mg/kg]	54 \pm 39	
Al [%]	0.027 \pm 0.013		Rb*) [mg/kg]	1.3 \pm 0.9	0.40
Ca [%]	21.7 \pm 1.3		Ti [mg/kg]	3.2 \pm 1.1	
Fe [%]	0.30 \pm 0.22	0.19	V [mg/kg]	4.7 \pm 4.3	
Mg [%]	11.9 \pm 1.2		Zn [mg/kg]	6.8 \pm 4.1	
Mg/Ca	0.53 \pm 0.13		$\delta^{13}\text{C}$ (PDB)	+ 0.86 \pm 1.65	
C ^{tot} [%]	12.05 \pm 1.09		$\delta^{18}\text{O}$ (PDB)	- 3.5 \pm 1.99	
Ba [mg/kg]	7.15 \pm 9.8	4.50	Sr/Ca \times 1000	0.40 \pm 0.47	
Co [mg/kg]	0.77 \pm 0.45	0.60			
Cr [mg/kg]	2.62 \pm 1.5		Dolomite (104) $^{\circ}\text{CuK}_{\alpha}$	30.95 \pm 0.05	
K [mg/kg]	125 \pm 110		Calcite (104) $^{\circ}\text{CuK}_{\alpha}$	29.73 \pm 0.15	
Mn [mg/kg]	116 \pm 34	98.00			
Na [mg/kg]	158 \pm 80				

*) Mean content Rb of 12 isotope dilution measurements.

seems to be in solid solution or in fluid inclusions in the carbonate phase as it correlates with Mg, Sr, $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ rather than with insoluble residue, Al or K-leachable content.

The Mn versus Sr/Ca evolution diagram (Fig. 3) shows that the stoichiometric low-Mg calcite sample (No. 184) formed from solutions enriched in Mn (Mn = 86 mg/kg) compared to pure seawater. The Sr-content (Sr/Ca \times 1000 = 2.55), however, is comparable to other early diagenetic low-Mg calcites (Text-Fig. 4). All dolomites are low in Sr but the Mn uptake varies due to the degree of recrystallization or due to the amount of Mn in solution at the time of recrystallization. Most of them contain about 100 mg/kg Mn. Few samples show additional Mn enrichment (> 150 mg/kg, e.g. sample No. 111, 198).



Text-Fig. 4.

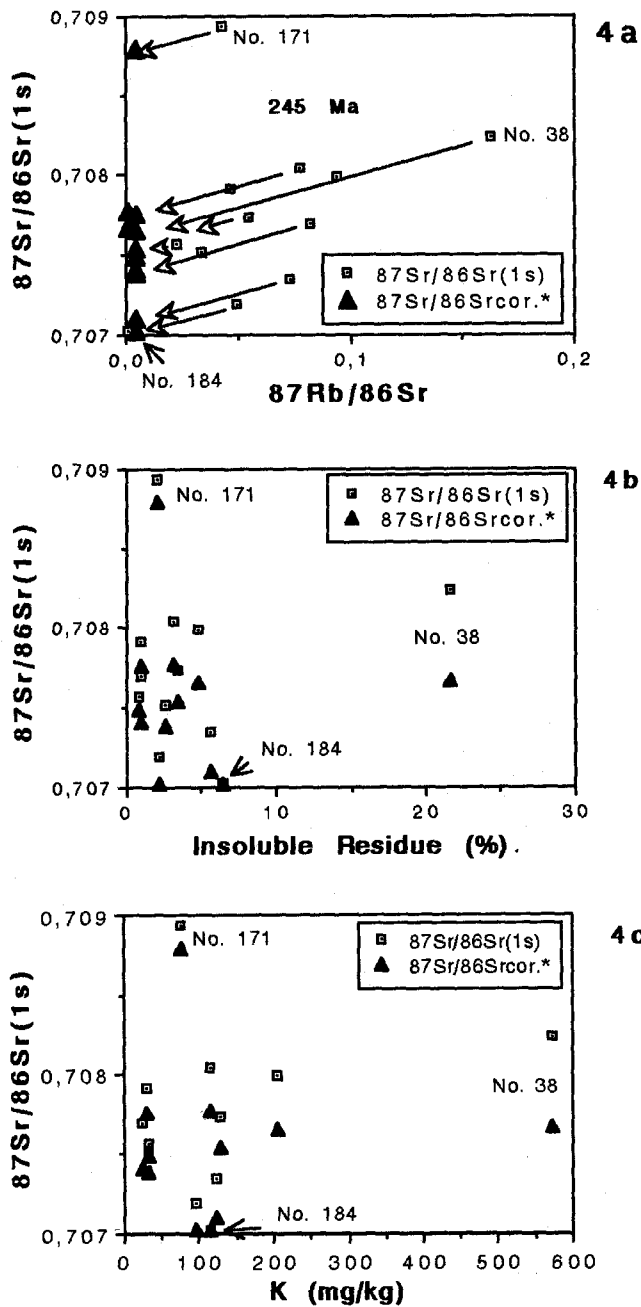
Mn content versus Sr/Ca ratio of Gartnerkofel core carbonate samples. The long arrow shows the diagenetic recrystallization trend (see also Fig. 5 and 6) as indicated in J. VEIZER (1983).

5. Rubidium-Strontium Isotopic Composition

The results of the Rb-Sr isotopic data are shown in Tabel 3 and in Text-Figs. 4–7. After a few measurements of the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios it was obvious that (with exception of one calcite sample [No. 184]), due to the low Sr content, the variable content of clay minerals, and the obvious partial recrystallization, the Gartnerkofel dolomites are only of limited value to establish

Table 3. Rb-Sr isotopic data of selected cation-leached carbonate samples (see "Analytical Techniques").

Sample No.	Depth [m]	Rb [mg/kg]	Sr [mg/kg]	$^{87}\text{Rb}/^{86}\text{Sr}$	$^{87}\text{Sr}/^{86}\text{Sr}$	$^{87}\text{Sr}/^{86}\text{Sr}$ corr.
38C	105.32	3.80	68	0.163	0.70824 \pm 9	0.70767
111C	184.72	1.19	44	0.078	0.70803 \pm 11	0.70777
					0.70806 \pm 7	
171C	207.14	1.22	82	0.043	0.70896 \pm 13	0.70879
184C	215.70	1.04	891	0.001	0.70695 \pm 13	0.70702
					0.70709 \pm 15	
198C	226.00	0.67	42	0.047	0.70786 \pm 9	0.70776
					0.70798 \pm 18	
200C	228.94	0.45	56	0.023	0.70757 \pm 8	0.70749
201C	229.12	1.70	59	0.082	0.70770 \pm 6	0.70741
204C	229.92	1.13	45	0.073	0.70735 \pm 15	0.70710
206C	231.25	1.16	61	0.055	0.70774 \pm 21	0.70754
207C	231.37	0.95	56	0.049	0.70720 \pm 18	0.70703
208C	231.72	1.71	53	0.094	0.70799 \pm 15	0.70766
215C	237.84	0.90	77	0.034	0.70744 \pm 9	0.70739
					0.70758 \pm 16	



Text-Fig. 5.
87Sr/86Sr versus 87Rb/86Sr (a), insoluble Residue (b) and 1 N HCl leached K (c) of Gartnerkofel core carbonate samples.

reliable 87Sr/86Sr seawater changes at the Permian-Triassic boundary. The Sr-isotopes are however, in combination with other isotopes and trace elements, good indicators of the diagenetic changes in this dolomite core.

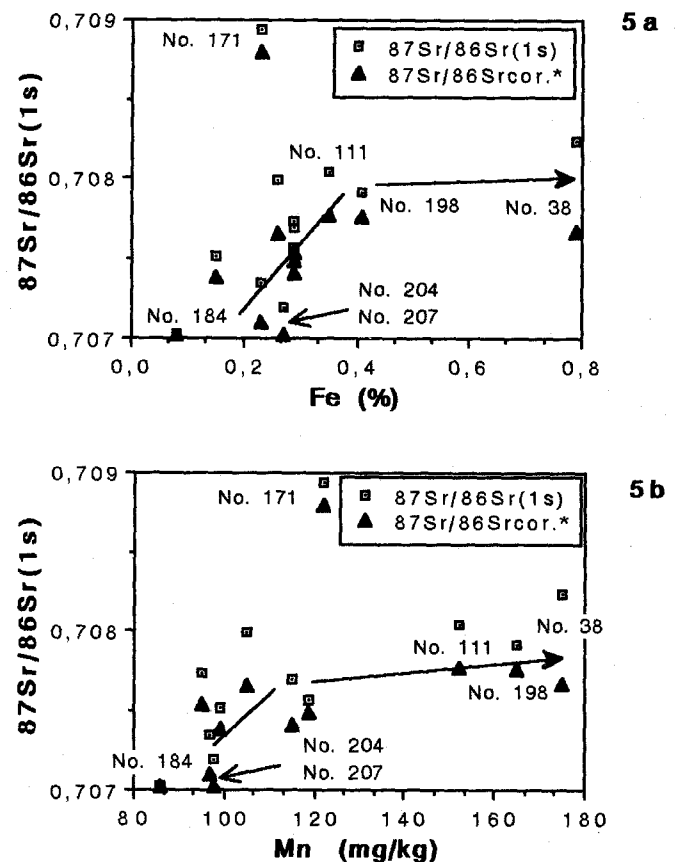
There is no correlation between the 87Sr/86Sr ratios and either the insoluble residues or the HCl leached K content (Text-Fig. 5b,c). Due to this fact, to the low mean residue and K values (Tab. 2) and to the gentle cation-exchange treatment (M. KRALIK, 1984), the radiogenic 87Sr* picked up during the dissolution of the carbonate is regarded as negligible. Only sample No. 38 (coarse grained Seis dolomite) with 22 % insoluble residue and 573 mg/kg HCl leachable K, seems to be partially influenced by radiogenic 87Sr* inherited from clays.

According to the findings of U. BRAND & J. VEIZER (1980) more or less well developed trends (Text-Fig. 4, 6a,b, 7a,b) of diagenetic recrystallization exist between

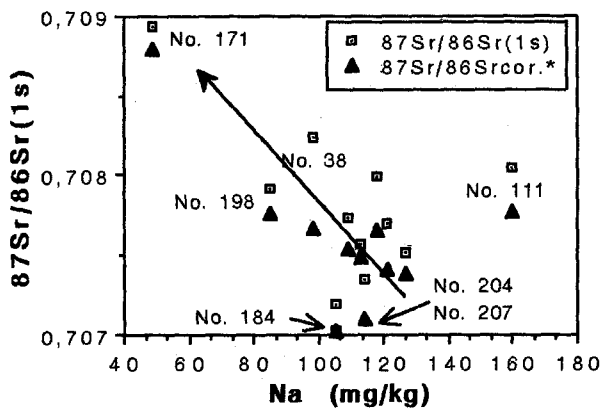
- the fine grained lowest Tesero dolomites (spl. No. 204 and 207) with Rb-corrected 87Sr/86Sr ratios (0.70710–0.70703) close to the assumed sea water values (W.T. HOLSER & M. MAGARITZ, 1987; D.G. BROOKINS, 1988) and
- the recrystallized coarse grained dolomites (spl. No. 38 and No. 171 [fault zone) with obvious radiogenic 87Sr* uptake (0.70767 and 0.70879).

This diagenetic trend is supported by Fe and Mn uptake (Text-Fig. 6a,b) and by Na, δ13C and a possible δ18O depletion (Text-Fig. 6a,b,c). The enrichment of Fe, Mn in dolomite sample No. 111 (Mazzin Member) indicates partial or complete diagenetic recrystallization due to geochemical evidence (Text-Fig. 4,6,7). If the depleted δ13C value ("soil CO2") and the relatively high Na content ("brined enrichment") can be interpreted as early diagenesis partially influenced by meteoric water at the third δ13C "low" (W.T. HOLSER et al., 1989, 186 m), could be corroborated by further specific investigations only. The calcite sample (No. 184, Mazzin Member) with a 87Sr/86Sr ratio (0.70702) close to assumed lowest Triassic seawater values, but depleted in δ18O (-7.44) coincides with the first δ13C "low" (220 m). These geochemical evidences can be interpreted best by recrystallization to low-Mg calcite in Sr- and Na-rich brines formed from meteoric waters typical for regression cycles.

The Sr-isotopes and the bulk carbonate chemistry is in good agreement with an early diagenetic dolomitiza-



Text-Fig. 6.
87Sr/86Sr versus Fe (a) and Mn (b) of Gartnerkofel core carbonate samples.

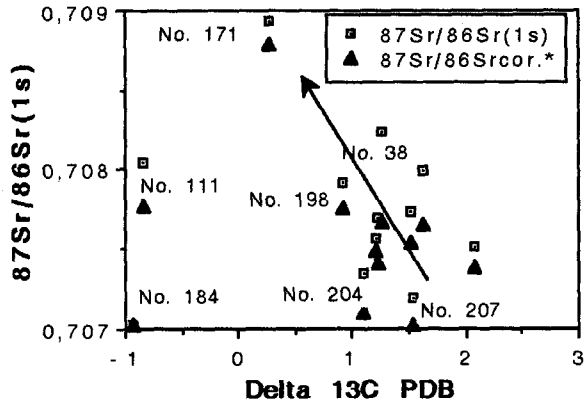


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tion with partial diagenetic recrystallization (radiogenic $^{87}\text{Sr}^*$ uptake from clay minerals) as fluids circulated through the platform sediments (K. BOEKELMANN & M. MAGARITZ, this volume). The "late" recrystallization of coarse dolomite close to a fault zone (No.171; 207,14 m) is supported by the highest measured $^{87}\text{Sr}/^{86}\text{Sr}$ ratio (0.70879).

Acknowledgement

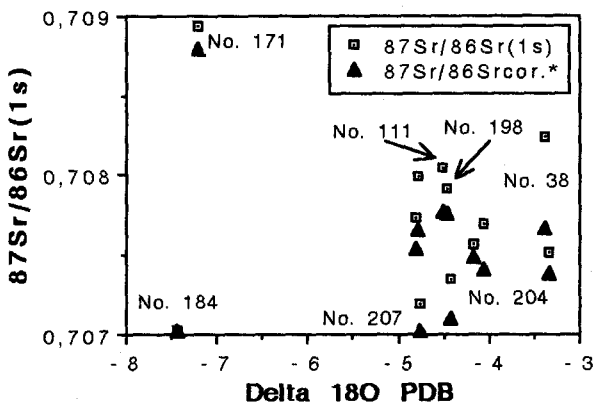
This work was partially supported by the Fonds zur Förderung der Wissenschaftlichen Forschung. I am indebted to Prof. Dr. W. FRANK, Dr. S. SCHARBERT and M. JELENC making available laboratory facilities, spike calibrations and laboratory support. A previous manuscript was considerably improved by critical reading of W.T. HOLSER.



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Text-Fig. 7. $^{87}\text{Sr}/^{86}\text{Sr}$ versus Na (a), $\delta^{13}\text{C}$ (b) and $\delta^{18}\text{O}$ (c) of Gartnerkofel core carbonate samples.

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