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Carbon and Oxygen Isotope Composition of Carbonates Accompanying Pb-Zn-Cu-As- and F-Mineralizations in Anisian Carbonates (Mid Triassic) in the Northern Calcareous Alps and the Drauzug, Austria*)

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With 7 Figures and 2 Tables

Österreich
Nördliche Kalkalpen
Drauzug
Mitteltrias
Anis
Gutensteiner Schichten
Muschelkalk
Kohlenstoff- und Sauerstoffisotope
Vererzungen (Pb, Zn, Cu, As)
Mineralisationen (F, Sr)

Contents

Zusammenfassung

Die Kohlenstoff- und Sauerstoffisotopenzusammensetzungen anisischer Karbonatgesteine (Mitteltrias) der Nördlichen Kalkalpen und des Drauzuges (Österreich) zeigen signifikante Variationen der δ^{13}C-Werte zwischen 0 und +4 ‰ (PDB) und der δ^{18}O-Werte zwischen +20 und +29 ‰ (SMOW). Unmetamorphe anisische Kalke sind durch hohe C- und O-Isotope gekennzeichnet; mit steigender anchizonaler Überprägung werden diese δ-Werte der Karbonatgesteine niedriger.

In den anisischen Karbonatgesteinen gibt es vier Hauptmineralisationstypen:

1) Bleiglanz, Zinkblende und Fluorit, feinkörnig sedimentär in partiell bituminösen Schichten.
2) Fluorit, Bleiglanz, Zinkblende und Cölestin als Kluftfüllungen in tektonisch beanspruchten Zonen in der Nähe von Evaporiten.
3) Eisenreiche Magnesite in Dolomiten in Zusammenhang mit Evaporiten.
4) Kupfer- und Arsenerze (Tennantit, Kupferkies, Auripigment) in Zusammenhang mit tektonischen Lineamenten (z. B. Möll-Linie in Kärnten).

Unter Berücksichtigung der C- und O-Isotopenergebnisse wird gefolgert, daß die Bleiglanz-, Zinkblende-, Fluorit- und Cölestinmineralisationen in den Klüften die Mobilisate der jeweiligen sedimentären Minerale sind, mobilisiert durch die NaCl-haltigen Wässer aus Evaporiten der unmittelbaren Umgebung. Die Differenzen der Isotopenzusammensetzungen zwischen Trägergestein und Kluftkarbonaten sind gering.

Die Bildungstemperaturen liegen zwischen 270 und 330°C; dies stimmt mit Untersuchungen an Flüssigkeitseinschlüssen in Fluoriten (Homogenisationstemperaturen) gut überein. Diese Temperaturen wurden während einer anchizonalen Überprägung der anisischen Karbonatgesteine erreicht.

Die Kupfer- und Arsenerze sind wahrscheinlich Produkte von Erzlösungen, welche möglicherweise aus den erzführenden Permsandsteinen herzuleiten sind, die die triassischen Karbonatgesteine stellenweise unterlagern. In diesen Fällen sind die Differenzen der Isotopenzusammensetzungen zwischen Trägergestein und erzbegleitenden Karbonatmineralen sehr groß.

Abstract

C- and O-isotope compositions of Anisian (Mid-Triassic) carbonate rocks (Northern Calcareous Alps and Drauzug, Austria) show significant variations of δ^{13}C-values between 0

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and +4 ‰ (PDB) and of $\delta^{18}O$-values between +20 and +29 ‰ (SMOW). Unmetamorphosed Anisian limestones have high C- and O-isotope values; with increasing anchizonal metamorphism the δ-values decrease.

Four main types of mineralizations occur in Anisian carbonates:

1) Fine grained, sedimentary galena, sphalerite and fluorite in more or less bituminous strata.
2) Fluorite, galena, sphalerite and celestine as fissure and cleft fillings in tectonic zones near evaporites.
3) Iron bearing magnesites in dolomites near by evaporites.
4) Cu-As-ores (tennantite, chalcopyrite, orpiment) related to major tectonic lines (e. g. Möll-line in Carinthia).

According to C- and O-isotopic investigations the galena, sphalerite, fluorite and celestine mineralizations in fissures were mobilized from sedimentary minerals by NaCl-bearing solutions derived from evaporites. The differences in isotopic compositions between host rocks and cleft carbonates are small.

The formation temperature lies between 270 und 330°C, which agrees with the results of fluid inclusion investigations of fluorites. These temperatures were reached during the anchizonal metamorphism of Anisian strata.

The Cu-As-ores are probably the products of ore bearing solutions, which possibly originated from the ore bearing Permian sandstones, which underly the Triassic carbonate rocks. The differences in isotope compositions between host rocks and accompanying carbonate minerals are large.

1. Introduction

Many small deposits of Pb, Zn, Cu and As accompanied by fluorite, magnesite and celestine occur in Anisian carbonates (Mid-Triassic) of the Northern Calcareous Alps (in Lower Austria, Styria, Upper Austria and Salzburg) and of the Drauzug (Carinthia); some of them were mined in the past century. These mineralizations have to be distinguished from the large and well known Pb-Zn-(Ba-F)ores in Ladinian and Carnian strata, e. g. Bleiberg (Carinthia), which are of economic and scientific interest (e. g. CERNY, 1984; SCHROLL, 1984; SCHULZ, 1985).

Furthermore, Pb-Zn-ores in Anisian carbonates are known from Yugoslavia (e. g. Topla [ŠTRUCL, 1981; DROVENIK, 1983; DROVENIK & PUNGARTNIK, 1987]), from Italy (e. g. Auronzo/Cadore [ASSERETO et al., 1976]), from Switzerland (Silberberg/Davos [KÖPPEL, pers. comm.]), from Western Germany (between Basel and Rottweil, and e. g. Wiesloch [HOFMANN, 1979; HILDEBRANDT & FLICK, 1984]) and from Poland (Upper Silesia [SASS-GUSTKIEWICZ et al., 1982]).

Mineral occurrences in Anisian carbonates are widespread in Austria and are situated in limestones and dolomites at the basis of Mid-Triassic sediments (GÖTZINGER, 1985). Twelve of the about 40 known occur-

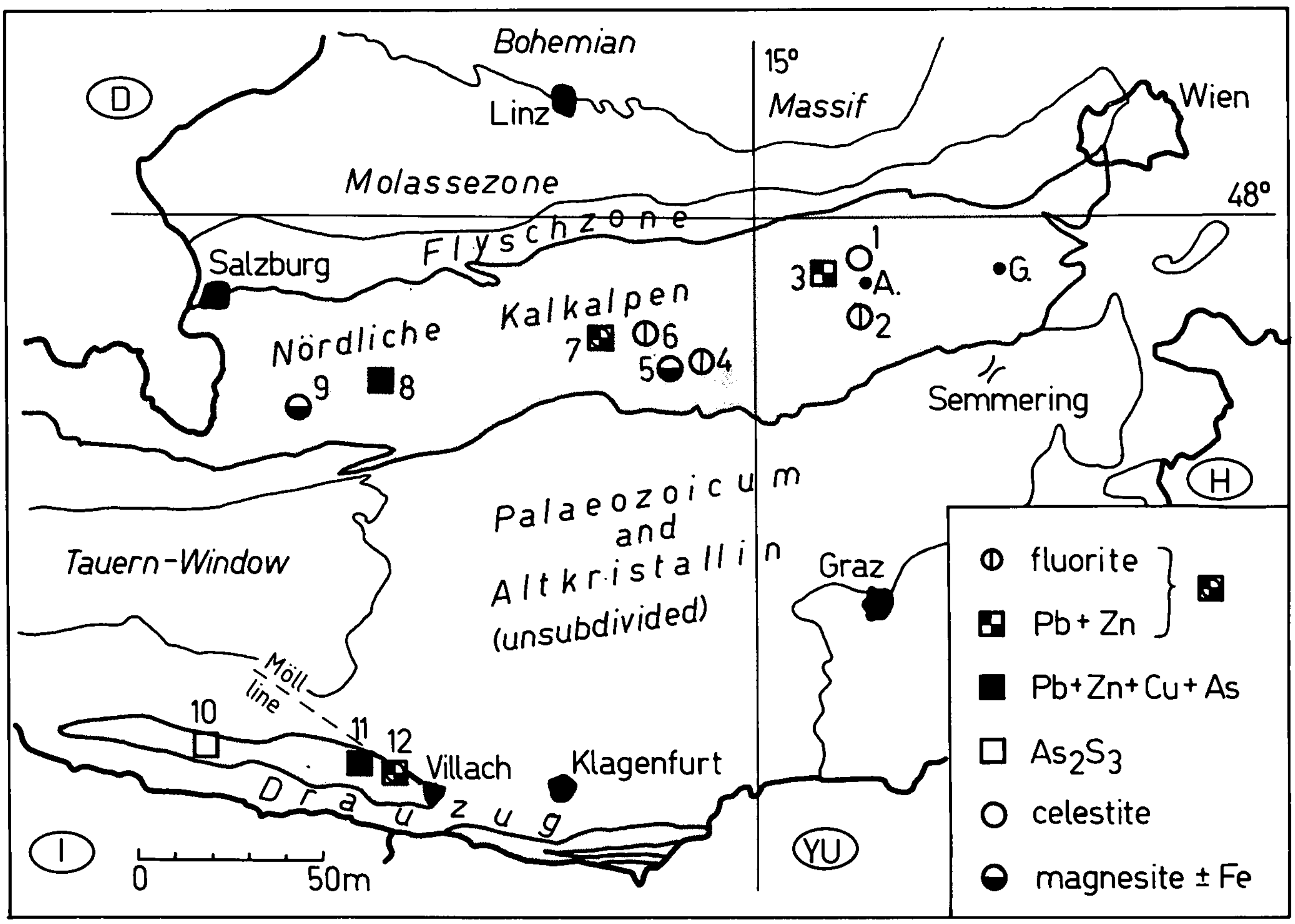

Fig. 1.
Geological sketch map of the Northern Calcareous Alps and the Drauzug in Austria with the mineral occurrences investigated.
1 = Schwarzenberg W Türnitz, Lower Austria; 2 = Halltal E Mariazell, Styria (HTM); 3 = Arzriedel near Trübenbach/Ötscher, Lower Austria (ARZ); 4 = Gams NE Hieflau, Styria (GA); 5 = Kaswassergraben NW Hieflau, Styria (KWG); 6 = Laussa-Platzl N St. Gallen, Styria (LP); 7 = Dambachtal E Windischgarsten, Upper Austria (DBT); 8 = Arikogel N Hallstatt, Upper Austria (ARK); 9 = Di(e)grub E Abtenau, Salzburg (DI); 10 = Stein SW Dellach/Drau, Carinthia (STD); 11 = Pöllan S Paternion, Carinthia (PÖ); 12 = Kellerberg NW Villach, Carinthia (KLB).
Type localities of Anisian Strata: A = Annaberg, G = Gutenstein (both in Lower Austria).

rences were selected for this C-O-isotope study and all important types of mineralizations are represented (see Fig. 1).

2. C- and O-Isotopes: Relations to Mineral Formation Processes

Investigations of the C- and O-isotope distribution between cleft minerals and the surrounding carbonate host rocks are of great interest. Similar δ-values possibly indicate similar formation conditions, e. g. a mineral mobilization within short distances by connate water. Large differences in δ-values may indicate that the mineralizations were formed under different conditions, for example at higher temperatures and/or in the presence of water of a different origin. Comparisons of δ-values are a very simple way to distinguish genetically different mineral formations. The isotopic compositions are mainly determined by the origin of the mineral forming fluids and by the formation temperatures (e. g. MC CREA, 1950; FRIEDMANN & HALL, 1963, FRITZ, 1969; OHMOTO & RYE, 1979; TAYLOR, 1979; KAPPEL & SCHROLL, 1982).

The aim of the following work is to compare the present genetic concepts with possible interpretations of C- and O-isotope distributions in calcite and/or dolomite of the fissure/cleft fillings and of host rocks. For genetic interpretations of (ore) minerals in fissures and clefts the differences of the δ-values for pairs of calcite – limestone (c-rc), calcite – rock dolomite (c-rd) and dolomite – rock dolomite (d-rd) are of interest (see e. g. FRITZ & SMITH, 1970; FRITZ, 1976).

3. Analytical Methods

Samples were ground in a hand mortar to ≤5 μm and an amount of 50 mg was reacted with 4 ml H_3PO_4 to produce CO_2. During preparation the reaction vessels were kept at a temperature of 25°C. Initially 85 % H_3PO_4 was used and the reaction time was 4 hours. Samples of a second batch were treated overnight with 100 % H_3PO_4 (COPLEN et al., 1983). The purpose of using 100 % phosphoric acid is to avoid water, which equilibrates with oxygen and thus influences the results.

Two samples were treated with both methods and the results differ only slightly; so the results of the two sample groups are comparable (values in ‰):

sample	$\delta^{13}C$ (PDB)		$\delta^{18}O$ (SMOW)	
	85 % H_3PO_4	100 % H_3PO_4	85 % H_3PO_4	100 % H_3PO_4
4	3.30	3.16	28.55	28.66
31	1.60	1.47	20.77	20.90

Mass spectrometric measurements were carried out on a Varian MAT 250 mass spectrometer. The ratios 44/45 and 44/46 were corrected for ^{17}O and other contributions according to GONFIANTINI (1970) to obtain the $\delta^{13}C$ and $\delta^{18}O$ values. $\delta^{18}O$ values of samples containing both calcite and dolomite were corrected according to dolomite content after PERRY & TAN (1972).

The precision of the mass spectrometer for gaseous samples is ±0.1 ‰ in routine work both for C and O. The sample preparation used in this work is an off-line method, the total error therefore being ±0.2 ‰ for C and O.

The δ-values relate to an isotopic ratio of a standard, the Δ-values are differences between δ-values of mineral pairs.

4. The Geological Setting

In the Northern Calcareous Alps the Anisian carbonate rocks are called "Gutensteiner Schichten"; for stratigraphy and lithological characterization see TOLLMANN (1966). Large outcrops of an important profile are located near Trübenbach/Ötscher (Fig. 1/3) and at Annaberg (Fig. 1/A.) in Lower Austria. The basis are Anisian evaporites (age indicated by means of their S-isotope ratios, GÖTZINGER & PAK, 1983). The type locality of Anisian rocks near Gutenstein (Fig. 1/G.) in Lower Austria was described by SUMMESBERGER & WAGNER (1971, 1972).

In the Drauzug (Gailtaler Alpen and Karawanken, Carinthia) the Anisian carbonates are known as "Alpiner Muschelkalk"; for stratigraphy see BECHSTÄDT (1978). In contrast to the Anisian carbonates of the Northern Calcareous Alps in the Drauzug a higher terrestrial-clastic influence is evident as well as the presence of restricted evaporitic basins.

Evaporites, to which some types of mineralizations are related, occur in both geological units: In the Northern Calcareous Alps thick Permian evaporites occur (cf. SCHAUBERGER, 1986) whereas Anisian evaporites are less important. In the Drauzug Permian evaporites play a minor role, however, important evaporitic beds of lower to middle Anisian age occur (STREHL, et al., 1980). A comprehensive presentation of the geology is given by TOLLMANN (1977).

5. The Mineralizations and their Host Rocks

In the Northern Calcareous Alps the host rocks of ore mineralizations are marls, limestones and dolomites, mostly located in tectonic zones near large evaporites of Permian age (cf. PAK & SCHAUBERGER, 1981).

In the Drauzug the ore mineralizations are located in the intermediate dolomitic level ("Dolomitisches Zwischenniveau"). Both, the Anisian carbonates of the Northern Calcareous Alps and of the Drauzug show a weak anchizonal metamorphism (≥270°C, 1.5–2 kbar; [NIEDERMAYR et al., 1984; GÖTZINGER, 1985; KRALIK et al., 1987]). For sedimentological descriptions of these Anisian sequences see SUMMESBERGER & WAGNER (1971, 1972), TOLLMANN (1976), BECHSTÄDT (1978) and GÖTZINGER et al. (1980).

Trace element contents of Anisian carbonate rocks are given in Table 1. The presence of very fine grained (≤0.1 mm) dispersed sphalerite, pyrite and/or marcasite, fluorite and coarser grained galena accounts for the high trace element values, significantly in dolomites. In some of these rocks organic matter obviously played a role during mineral formation.

Table 1.
Average contents of some trace elements in limestones and dolomites of the Northern Calcareous Alps and the Drauzug (only Gailtaler Alpen: WARCH, 1984; about Karawanken see CERNY, 1977, 1978).
EDX-, XRF-, AAS- and ICP-analyses; F-analyses with an ion-sensitive electrode; values in ppm.

	Northern Calcareous Alps		Drauzug	
	limestones (n = 9)	dolomites (n = 11)	limestones (n = 3)	dolomites n = 13)
Pb	90 ± 40	150 ±100	80± 26	68± 35
Zn	10 ± 9	120 ± 85	253±230	123± 115
Cu	3.5± 1,8	2.7± 0.8	≤10	≤10
Fe	720 ±600	1200 ±480	2450±490	3550±2800
Mn	30 ± 10	70 ± 20	790±650	730± 660
Sr	860 ±600	200 ±110	310±140	63± 29
F	260 ±180	470 ±320	n.d.	n.d.

Four main types of mineralizations occur in Anisian carbonates:

1) Fine grained ores in (bituminous) strata consisting of galena, sphalerite, fluorite and celestine;
2) Ore mineralizations in fissures and clefts
   a) fluorite (± traces of galena)
   b) galena and sphalerite;
3) Cu-As-ores (tennantite, chalcopyrite; orpiment, realgar) in clefts, veinlets and dolomitization zones related to major tectonic lines;
4) Magnesites and their host rocks near evaporites – Hall type magnesites according to POHL & SIEGL (1986).

6. C- and O-Isotope Data and their Interpretation

C- and O-isotope values are listed in Table 2. The following signs and abbreviations are used:

calcite in fissures and clefts .... (c) ▲
dolomite in fissures and clefts .... (d) ◆
limestone, rock calcite .... (rc) ●
dolomite, rock dolomite .... (rd) ■

Numbers in italics are sample numbers.

6.1. Anisian Carbonate Rocks Locally with Fine-Grained Ores

The $\delta^{13}C$ (PDB) values of the Anisian carbonate rocks vary between 0 and +4 ‰, which is characteristic for Triassic sediments (VEIZER & HOEFS, 1976); the $\delta^{18}O$-values of most Anisian carbonate rocks vary from −10 to −5 ‰ (PDB), or +20.6 to +25.7 ‰ (SMOW); see Figs. 2 and 3.

At some occurrences the isotopic compositions of different samples of limestones are similar. But limestones and dolomites from the same occurrence are obviously not in equilibrium (LP, HTM), see Figs. 3–5. So the dolomitization probably took place in the presence of different solutions (see e. g. FRIEDMANN & HALL, 1963; FRITZ & SMITH, 1970; MATTHEWS & KATZ, 1977), which may be the result of a late diagenetic dolomitization (BAUSCH & HOEFS, 1972).

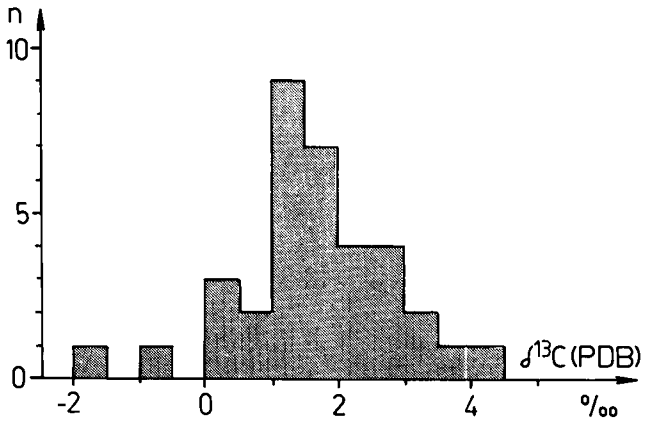

Fig. 2.
Histogram of $\delta^{13}C$ (‰, PDB) distribution in Anisian carbonate rocks (limestones and dolomites).

Unmetamorphosed Anisian limestones (e. g. sample nr. *5**) show high C- and O-values; however, with increasing grade of anchizonal metamorphism C- and O-values decrease. This might be the result of an isotopic exchange with migrating fluids and/or silicates during metamorphic events. The intensity of metamorphism was detected by determinations of illite crystallinity and characteristic silicate minerals in the acid residue (GÖTZINGER, 1985 and unpublished data).

Fine grained galena, sphalerite, fluorite and celestine are dispersed in Anisian sediments (mostly in dolomites), together with pyrite and/or marcasite. These minerals are locally concentrated in bituminous parts; a sedimentary origin seems to be very likely. Lead, zinc and fluorine could derive from leaching of crystalline rocks as indicated by Pb-isotopes (KÖPPEL & SCHROLL, 1985, 1988; KÖPPEL, pers. comm. 1986).

Sample nr. *21, 38, 64* are ore bearing dolomites with fine grained, dispersed galena (± pyrite/marcasite and sphalerite). Two of them show very similar C- and O-isotope values with $\delta^{13}C$ values slightly higher than those of other rocks with $\delta^{18}O$ near +22 ‰. Since the ore formation did not significantly change the isotope ratios, it is suggested that the ore minerals are the result of synsedimentary enrichment and crystallization (cf. e. g. DOLENEC et al., 1983).

6.2. Ore Mineralizations as Fissure and Cleft Fillings

Galena, sphalerite, fluorite and celestine with calcite and/or dolomite occur as fissure fillings in tectonized limestones or dolomitization zones in the vicinity of evaporites. According to REE-contents and REE-distribution in fluorites these mineralizations are mobilizations of the sedimentary enrichments (see above).

Fluorite (±traces of galena)

Nine mineral pairs (cleft carbonate – host rock) were selected from a small area (about 100 m²) of one outcrop (Laussa-Platzl, LP) to test for possible variations of the $\delta^{13}C$ and $\delta^{18}O$-values (Fig. 4).

*) Specimen nr. *4* is a calcite in paragenesis with coexisting celestine in a fissure filling from Schwarzenberg, Lower Austria (cf. HAGENGUTH et al., 1982).

Table 2.
C- and O-isotope compositions of Anisian carbonate minerals and rocks.
c = cleft calcite; d = cleft dolomite; rc = limestone; rd = rock dolomite.

sample nr.	mineral rock	locality	accompanying minerals	$\delta^{13}C$ (‰, PDB)	$\delta^{18}O$ (‰, SMOW)
2	d	Arzriedel	galena, sphalerite	1.70	23.21
20	rd	Arzriedel	——	1.94	25.29
3	rd	Annaberg-Hocheck	acanthite	2.05	24.89
4*)	c	Schwarzenberg	celestine	3.30	28.55
				3.16	28.66
5	rc	Schwarzenberg	——	3.70	31.75
21	rd	Schwarzenberg	sedimentary galena and pyrite	2.72	21.75
6	c	Laussa-Platzl	fluorite	1.13	22.47
7	c	Laussa-Platzl	fluorite	0.24	22.28
8	c	Laussa-Platzl	fluorite	0.70	24.00
9	rc	Laussa-Platzl	——	1.47	24.07
10	d	Laussa-Platzl	——	1.51	23.44
11	rd	Laussa-Platzl	——	2.51	25.97
12	c	Halltal	fluorite	−0.48	21.89
13	rc	Halltal	——	1.71	20.31
14	rd	Halltal	——	1.53	23.12
15	rc	Gams (nr. 3376)	fluorite	4.25	28.77
16	c	Gams (Dr. F.)	fluorite	1.45	19.71
17	rc	Gams (Dr. F.)	——	1.74	20.09
18	c	Stein/Dellach	orpiment	1.59	19.04
19	rc	Stein/Dellach	——	2.79	24.09
25	c	Arikogel	pyrite	−3.60	17.38
26	d	Arikogel	sphalerite	2.62	25.64
27	rd	Arikogel	——	2.50	27.97
28	d	Kellerberg	galena, fluorite	1.65	19.49
29	rd	Kellerberg	——	1.64	20.50
64	rd	Kellerberg	sedimentary galena	2.58	21.55
31*)	c	Kellerberg motorway	(mylonite)	1.60	20.77
				1.47	20.90
32	rc	Kellerberg motorway	——	2.84	27.04
33	c	Gratschenitzen (road)	cleft	−1.21	14.44
34	rc	Gratschenitzen (road)	——	−1.93	24.28
35	d	Pöllan	tennantite, chalcopyrite	−0.12	18.79
36	rd	Pöllan	——	0.47	19.90
37	(r)d	Pöllan	dolomitization zone	0.47	19.93
38	rd	Pöllan	sedimentary galena	0.11	22.88
39	c	Dambachtal	fluorite, galena	0.43	22.64
40	rc	Dambachtal	——	1.22	21.24
45	c	Laussa-Platzl	fluorite	0.86	23.12
46	rc	Laussa-Platzl	——	1.33	22.54
47	c	Laussa-Platzl	fluorite	0.90	23.08
48	rcd 1 : 1	Laussa-Platzl	——	1.44	23.16
49	c	Laussa-Platzl	fluorite	0.21	22.71
50	rc	Laussa-Platzl	——	1.28	22.46
51	c	Laussa-Platzl	fluorite	0.20	22.56
52	rc	Laussa-Platzl	——	1.26	22.24
53	c	Laussa-Platzl	fluorite	0.75	22.75
54	rc	Laussa-Platzl	——	1.13	23.02
55	d	Laussa-Platzl	calcite	1.92	24.35
56	c	Laussa-Platzl	dolomite	0.78	22.84
57	rd	Laussa-Platzl	——	1.47	24.86
58	d	Pöllan	tennantite	−0.68	18.34
59	c	Pöllan	azurite	−5.50	21.11
60	rd	Pöllan	——	1.22	20.59
61	d	Pöllan	azurite	−0.25	19.35
62	rd	Pöllan	——	0.81	20.57
63	rd	Pöllan	bituminous	1.43	24.07
Tb 11	rc	Trübenbach	sedimentary fluorite	2.02	24.23
4201	rd	Annaberg-Spindelhof	——	−0.63	22.12

*) first line: 85 % H_3PO_4; second line: 100 % H_3PO_4.

In most cases (specimens nr. *45–57*) the δ-values are very similar, especially the $\delta^{18}O$-values. The average differences Δ (c-rc) and Δ (d-rd) are for carbon 0.66 ±0.32 ‰ and for oxygen 0.26 ±0.17 ‰. The range of Δ (c-rd) values is much bigger, especially for oxygen: 1.6 to 2.5 ‰. However, the pairs calcite – limestone define a restricted field (see also Fig. 5), which serves as a reference field of C- and O-isotope variations in mobilization zones within Anisian carbonates.

Fig. 5 shows the C- and O-isotope values of genetically similar fluorite-calcite occurrences in fissures and clefts (Halltal, HTM; Dambachtal, DBT; Gams, GA; Kellerberg, KLB). The values are similar to those of Laussa-Platzl (LP). In all these occurrences small amounts of galena are present, sphalerite is scarce.

Mobilizations range from a few tens of centimeters to a few tens of meters as shown at the occurrences of Laussa Platzl and at Kellerberg (GÖTZINGER, 1985). In the close vicinity of all mineralizations Permian evaporites occur, from which NaCl-rich solutions may have originated and which mobilized metals and minerals. Fluorite crystals often contain small fluid inclusions with NaCl crystals (GÖTZINGER & WEINKE, 1984; GÖTZINGER, 1984). Homogenization temperatures of primary inclusions lie between 270 and 330°C (in preparation).

Galena and Sphalerite

Galena and sphalerite ores occur predominantly in dolomite bearing veinlets and clefts or in dolomitization zones; the occurrences Dambachtal (DBT) and Kellerberg (KLB) contain only galena and fluorite. Fig. 6 shows the C- and O-isotope data. It is remarkable that the $\delta^{13}C$-values of each occurrence lie within a narrow range. The cleft dolomites show slightly lower $\delta^{18}O$-values than the corresponding rock dolomites. This might indicate that the vein dolomite with ore minerals precipitated at a higher temperature than the rock forming carbonates (occurrences ARK, ARZ, KLB). There are no convincing indications of an influence of meteoric water during mineral formation.

At Kellerberg (KLB) dolomites contain fine grained galena (*64*); and dolomites (*29*) contain mobilized galena with dolomite in clefts (*28*).

The original ore bearing dolomite shows higher isotope ratios than those in mobilization zones. The decreasing ratios might be the product of solutions resulting from anchizonal metamorphism.

Decreasing isotope ratios are also observed at Pöllan (PÖ), where bituminous limestones (*63*) occur together with fine grained galena bearing dolomites (*38*).

The very low Δ-values of carbon isotopes and the Δ-values for oxygen isotopes (1.05 to 2.33 ‰) between cleft carbonates and host rocks suggest mineral mobilization from the surrounding rocks during anchizonal metamorphism as described for the fluorite mineralizations. According to the Pb and Zn contents of Anisian carbonate rocks (Table 1), this explanation of ore formation is obvious and not problematic.

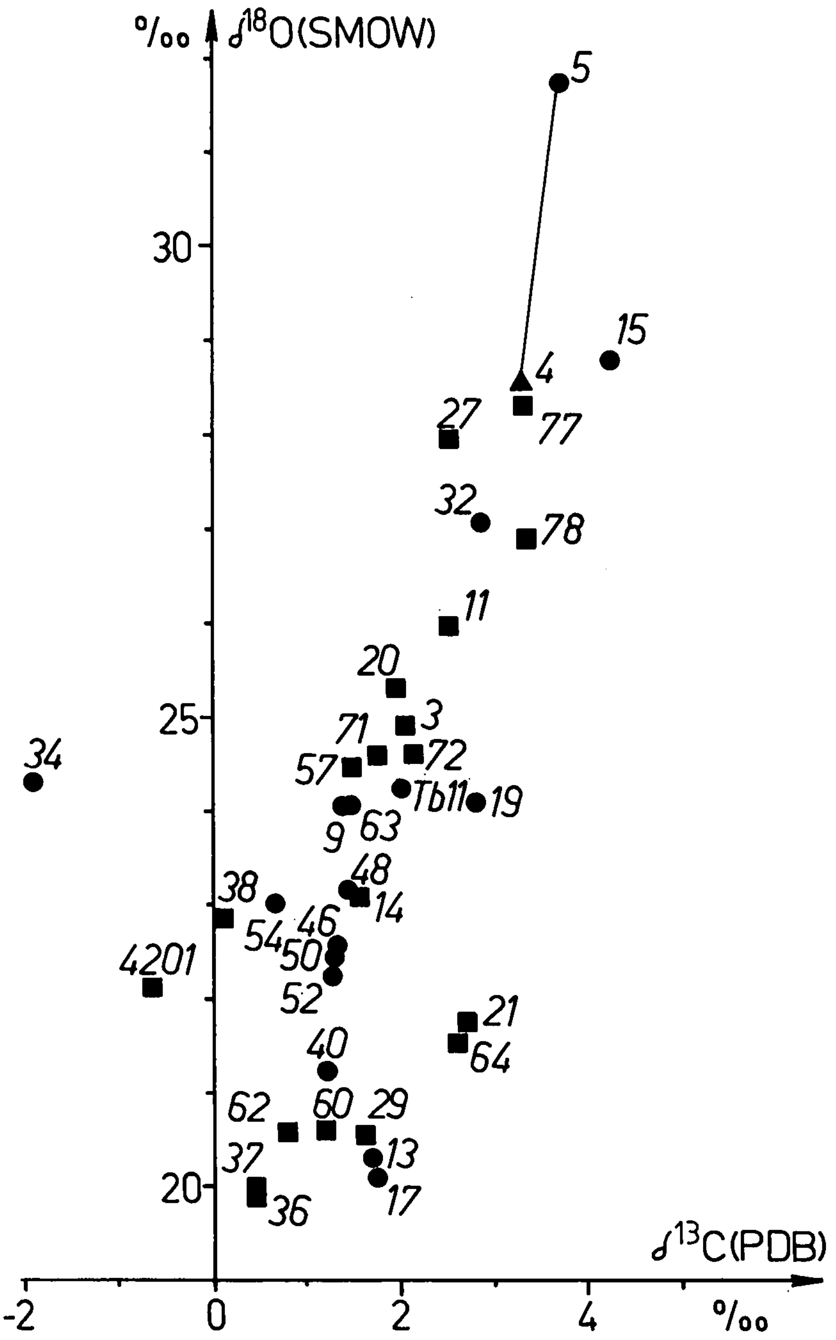

Fig. 3.
A $\delta^{18}O$ (‰, SMOW) versus $\delta^{13}C$ (‰, PDB) diagram of isotopes distribution in Anisian carbonate rocks.
● = limestone; ■ = dolomite; ▲ = calcite.

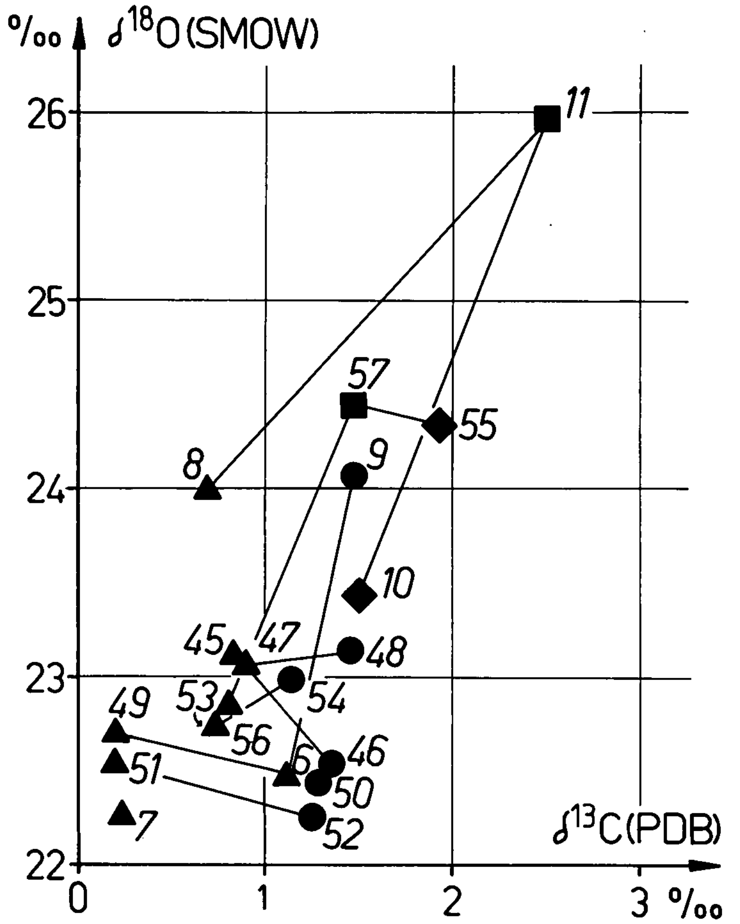

Fig. 4.
Comparison of the isotopic composition of cleft calcites (▲) and cleft dolomites (◆) with their host rocks, limestones (●) and dolomites (■) of the fluorite occurrence of Laussa-Platzl in Styria. Lines indicate pairs of cleft and hostrock carbonates.

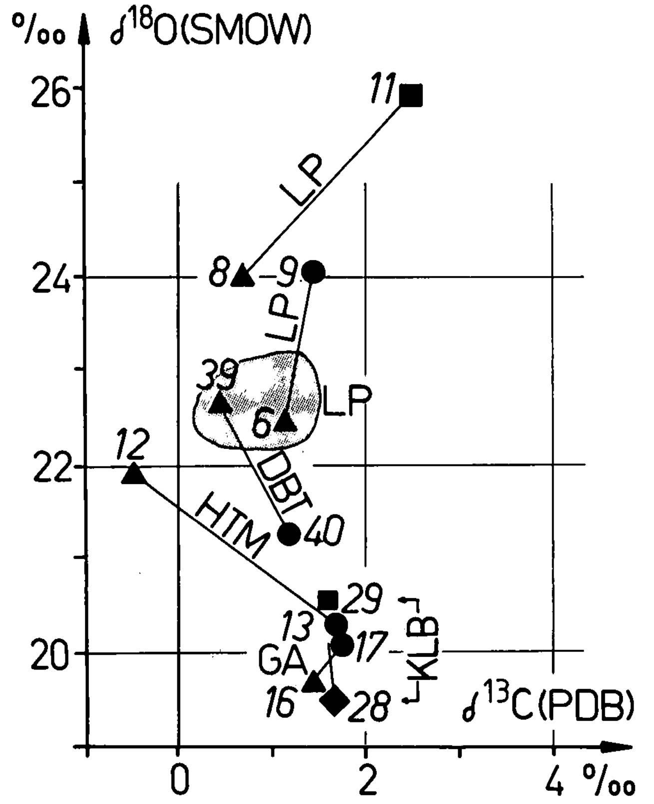

Fig. 5.
The isotopic composition of cleft and host rock carbonates of five fluorite occurrences.
The dark field represents the specimens nr. 45–54, 56 of Fig. 4.
DBT = Dambachtal E Windischgarsten (Upper Austria); GA = Gams NE Hieflau (Styria); HTM = Halltal E Mariazell (Styria); KLB = Kellerberg NW Villach (Carinthia); LP = Laussa Platzl N St. Gallen (Styria).

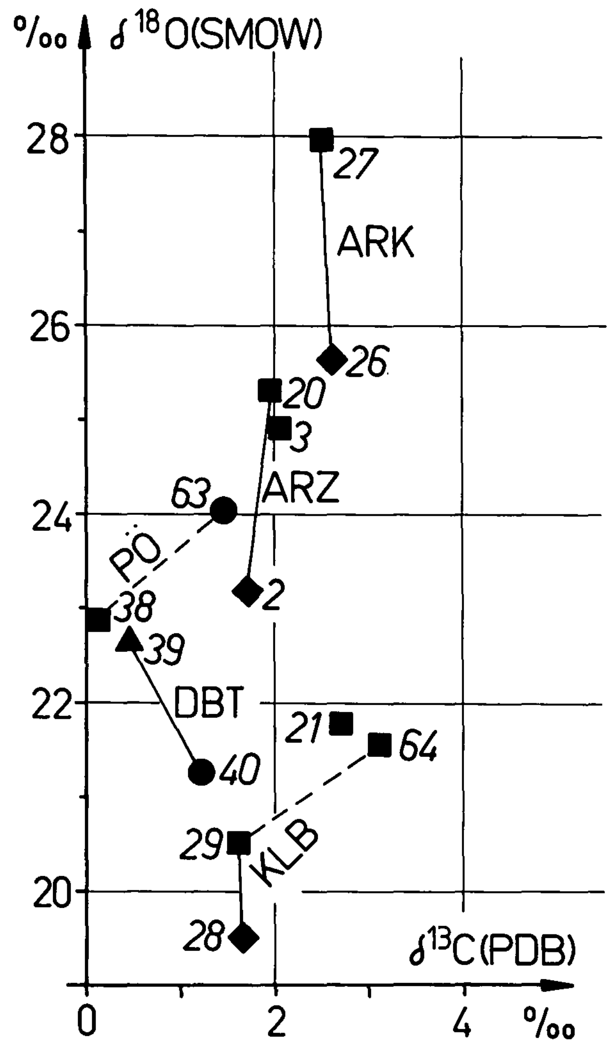

Fig. 6.
The isotopic composition of cleft and host rock carbonates of five galena-sphalerite occurrences.
ARK = Arikogel N Hallstatt (Upper Austria); ARZ = Arzriedel near Trübenbach/Ötscher (Lower Austria); DBT = Dambachtal E Windischgarsten (Upper Austria); KLB = Kellerberg NW Villach (Carinthia); PÖ = Pöllan S Paternion (Carinthia).

6.3. Cu-As-ores in Clefts, Veinlets and Dolomitization Zones

Tennantite, chalcopyrite and cuprite (with azurite and malachite) occur in dolomite veins and in dolomitization zones. Locally sedimentary galena, which is not cogenetic with the Cu-paragenesis, is also present. An origin of the Cu from the host rocks appears to be unlikely in the view of their low Cu concentrations (Table 1). It seems more likely that Cu and As were supplied from Permian sandstones (e. g. Präbichl-Schichten, Grödener Sandstein), where Cu-As-ores are known to exist (BAUMGARTNER, 1976; HADITSCH & MOSTLER, 1982; MOSTLER et al., 1982; NIEDERMAYR & NIEDERMAYR, 1983; WOPFNER et al., 1983). Most of the mineral pairs of this group (cleft carbonate/host rock) show high or very high Δ-values for carbon and especially for oxygen isotopes. These data and the geological situations suggest an origin of the ore bearing solutions (probably of higher temperature) from other geologic horizons (Fig. 7). One characteristic example is the pyrite and chalcopyrite ore mineralization of Arikogel near Hallstatt (ARK). Figs. 6 and 7 show that two stages of ore mineralization are discernible. At the stratigraphic basis of the Northern Calcareous Alps many chalcopyrite-siderite occurences of the type Hirschwang (Lower Austria [BAUMGARTNER, 1976]) are known in the Permian Prebichl-Schichten. Possibly, parts of this Cu-ores were mobilized into Anisian carbonate rocks.

A more complex situation prevails in the mineralizations of the Drauzug near Pöllan (Carinthia), which is situated closely to the south of the tectonic Möll-line. The original rocks are more or less bituminous limestones (nr. *63*). In some dolomitic intercalations fine grained galena ore occurs (nr. *38*). The Δ-values of carbon and oxygen of the two rock samples are nearly equal: 1.2 ‰. The host rock dolomites of the Cu-As-ore bearing clefts and veins (Nr. *36, 37, 60, 62*) show very similar δ-values for C and O; average values are: $\delta^{13}C = 0.74 \pm 0.36$ ‰; $\delta^{18}O = 20.25 \pm 0.38$ ‰. The difference to the fine grained galena bearing dolomite (nr. *38*) is large for $\Delta^{18}O$: 2.63 ‰. So it is evident that within this occurrence three carbonate types are discernible:

a) Bituminous limestone.
b) Dolomite with sedimentary galena.
c) Dolomite with clefts containing dolomite and ores.

Dolomites of the ore bearing clefts and veins show variable Δ-values with respect to their host rocks. The Δ (d-rd)-values for carbon lie between 0.58 and 1.90 ‰ and for oxygen between 1.14 and 2.25 ‰. In addition some clefts contain calcite which may have crystallized late from solutions containing meteoric water (nr. *59*).

North of the Drauzug NW Villach a mylonitic zone near Kellerberg (KLB-MY) is probably related to the important tectonic Möll line (Fig. 1). Large outcrops were exposed during the construction of the motorway. These mylonites contain veinlets, fissures and clefts filled with calcite and locally galena, celestine, baryte and secondary minerals (NIEDERMAYR et al., 1986; PRASNIK, 1987). Some parts are rich in liquid and solid bitumina. Also at the road near Gratschenitzen (GRT-CL) calcite in fissures and clefts occurs. All these mineral pairs (c-rc) show high $\Delta^{18}O$-values. In both cases the calcites show lower $\delta^{18}O$-values than their host rocks and thereby indicate the presence of thermal solutions which circulated along the Möll line.

Near Stein/Dellach, Drau-Valley (Carinthia) orpiment, realgar and calcite occur as fissure fillings in the Alpiner Muschelkalk. This mineralization also shows similar C- and O-isotope differences as observed in the Kellerberg mylonites (KLB-MY). So this orpiment mineralization might be genetically related to a vein type ore mineralization such as the stibnite – arsenopyrite – mercury veins of the Kreuzeck-Gruppe NW of Stein (CERNY et al., 1981; GÖTZINGER & PAK, 1983).

7. Concluding Remarks

C- and O-isotope investigations confirm the evidence of four different types of mineralizations in Anisian carbonate rocks:

❶ A primary sedimentary enrichment of galena, sphalerite, fluorite and celestine, fine grained dispersed within Anisian carbonate rocks. These minerals are

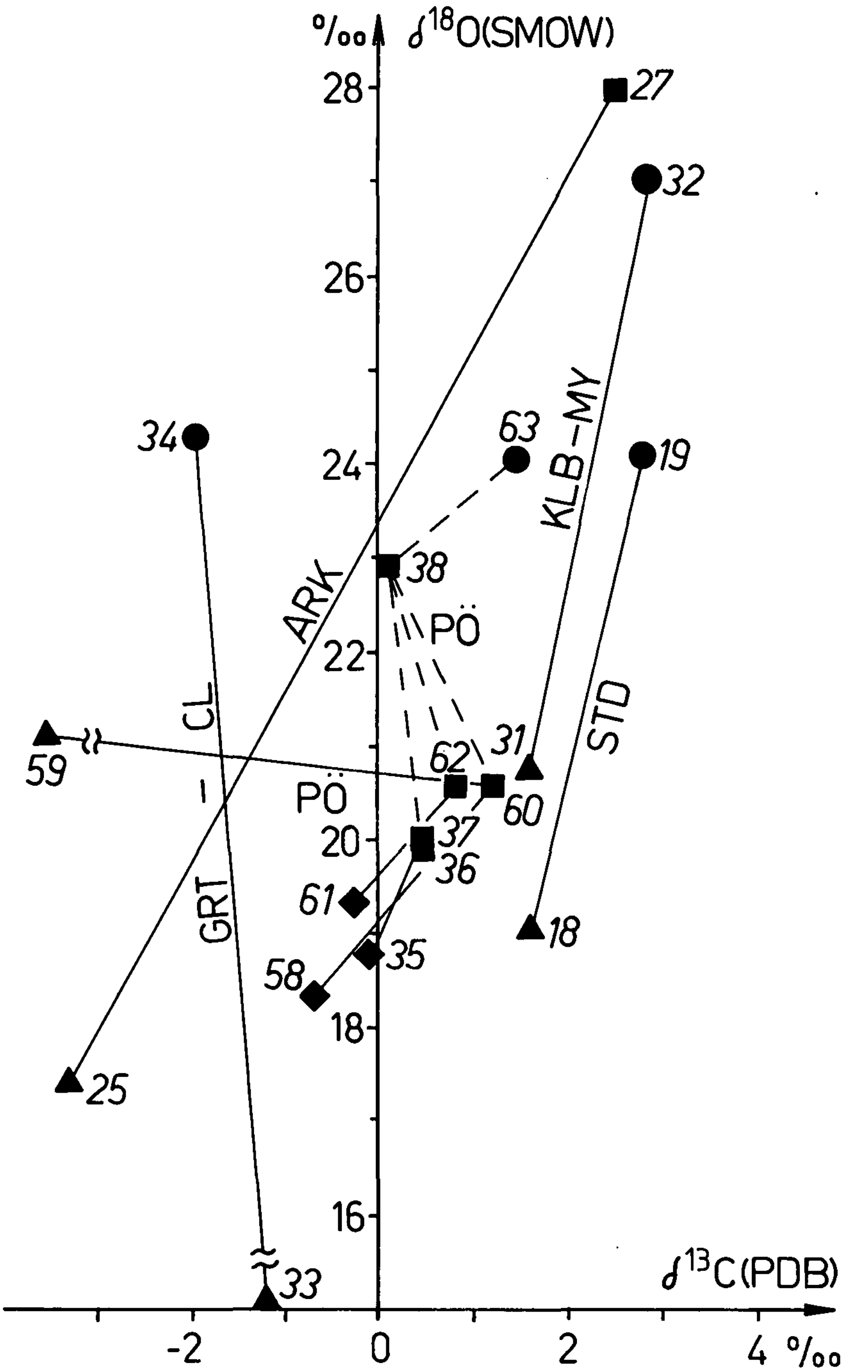

Fig. 7.
The isotopic composition of cleft and host rock carbonates of Cu±As-bearing mineralizations and in mylonites.
ARK = Arikogel N Hallstatt (Upper Austria); GRT-CL = Gratschenitzen SW Paternion (Carinthia); KLB-MY = Kellerberg motorway NW Villach (Carinthia); PÖ = Pöllan S Paternion (Carinthia); STD = Stein SW Dellach/Drau (Carinthia).

syngenetic; in some occurrences they are coarser grained (up to 1 mm) caused by high fluid activity of formation waters (e. g. Kellerberg).

❷ A mobilization of sedimentary galena, sphalerite, fluorite and celestine from Anisian carbonate rocks into tectonic fissures and clefts. According to fluid inclusions in fluorite, the solutions are rich in NaCl and yield homogenization temperatures between 270 and 330°C. This indicates a formation of fluorite (and accompanying minerals) during anchizonal metamorphism. The NaCl bearing solutions are derived from evaporites, where locally cubic caverns, typically for halite, are found in chlorite bearing quartzites.

❸ A magnesite formation in Anisian carbonate rocks – this is a theme of a separate article (GÖTZINGER et al., 1990).

❹ A formation of chalcopyrite, tennantite and orpiment by Cu- and As-bearing solutions. These solutions are derived from e. g. Permian strata; in relation to deep tectonic lines, especially in the Drauzug. The time of formation and the origin of the solutions are not known, but they are related to tectonic events and to accompanying dolomitization processes.

Finally, within some Permian evaporites basic volcanic rocks occur. Some of them contain numerous primary and secondary Cu-minerals (KIRCHNER et al., 1981). A genetic connection to the Cu-mineralizations in the Anisian strata is possible.

The Anisian Pb-Zn-deposits show similarities to the worldwide occurring Mississippi Valley Type Pb-Zn-deposits (see e. g. KISVARSANYI et al., 1983; SVERJENSKY, 1986). Considering the C- and O-isotope compositions, similarities are evident to the Pb-Zn-deposits of Bleiberg (Carinthia) and Lafatsch (Tyrol) (SCHROLL, 1985).

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