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Sr, O, and C Isotope Study of the Brixlegg Barite Deposit, Tyrol (Austria)

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Abstract

An investigation of Sr, C, and O isotope variation in the Brixlegg barite deposit in the Western Graywacke zone (Upper Austroalpine unit; eastern Alps) demonstrates the possibility that variations in Sr isotope ratios between mineralized and nonmineralized zones in epigenetic carbonate-bound ore deposits can be used both as a genetic indicator for the type of mineralizing fluid and as a prospecting tool. Similar variations in O and, to a lesser extent, C isotope ratios are evident but are less powerful aids for exploration.

An epigenetic model for the deposit studied is supported by isotopic ratios determined on barite and its dolomite host rock (including some evaporite relics). The mineralization is attributed to formation waters and/or metamorphic fluids of Hercynian age with underlying metaclastic strata being the most probable source of the Ba and Sr.

Introduction

INVESTIGATION of isotopic characteristics of ore mineralization and gangue minerals has become increasingly important in the study of ore-forming processes. Barite has proven to be an excellent target for Sr isotope studies because of its generally extremely low Rb/Sr ratio, which consequently provides the opportunity to obtain initial isotopic ratios. By means of these ratios evidence for the source of the mineralizing fluids, as well as for the possible source of the Ba, has been obtained (e.g., Kessen et al., 1981; Barbieri et al., 1982, 1984; Lange et al., 1983; Dill and Carl, 1987).

In carbonate-bound ore deposits, comparison between the isotopic composition of ore minerals and cogenetic gangue minerals and that of their host rocks has provided valuable information regarding their genesis (Frimmel, 1988). Zones of isotopic alteration detected within carbonate host rocks in the vicinity of Fe mineralizations of the Eastern Graywacke zone (Frimmel, 1988) indicate the possibility that isotopes, especially Sr, can be used as tracers for locating additional orebodies.

The Brixlegg barite deposit is part of an ore district in the Western Graywacke zone (Upper Austroalpine unit), which is characterized by barite-tetrahedrite mineralization. These deposits are characteristically associated with a massive carbonate complex of Devonian age, the Schwaz dolomite. Although the tetrahedrite was mined extensively at several localities between Schwaz and Brixlegg in the past, the interest of the mining industry is now focused on barite, which occurs in an exceptionally pure grade. The only presently known economic deposit is at the Großkogel mine near Saint Gertraudi, some 3 km south-southwest of Brixlegg (for location see Figs. 1 and 2).

Genetic models proposed for these strata-bound barite sulfide mineralizations include epigenetic-hydrothermal ones (Vohryzka, 1968; Tufar, 1979) as well as syngenetic-sedimentary processes (Schulz, 1972; Schroll, 1979), while Mostler (1984) relates them to late Paleozoic karstification. Observations by Gstrein (1979) in the Schwaz area indicate a syngenetic origin of the primary sulfide mineralization. The genesis of the barite, however, has remained problematical.

An Sr isotope study on this deposit assists in determining the source of the mineralizing solutions in the Paleozoic mineral province of the Austroalpine complex. In order to gain an economically viable tool for further prospecting, the study has been extended to C and O isotopes, because measurement of these stable isotopes is normally less expensive than that of Sr isotopes. However, Sr isotopes provide a more direct geochemical link with Ba and hence the presence of an ore deposit.

Geologic Setting

The mineralized Schwaz dolomite (Table 1) represents shallow water and partly supratidal sediments of a preorogenic carbonate platform within the early Paleozoic series of the Upper Austroalpine Graywacke zone. Syndepositional erosion of parts of the platform is indicated by several breccia layers, with reworked dolomite clasts within the dolomite complex. Evaporitic horizons are recorded by remnants of largely remobilized anhydrite layers.

The lower parts of the Schwaz dolomite have been

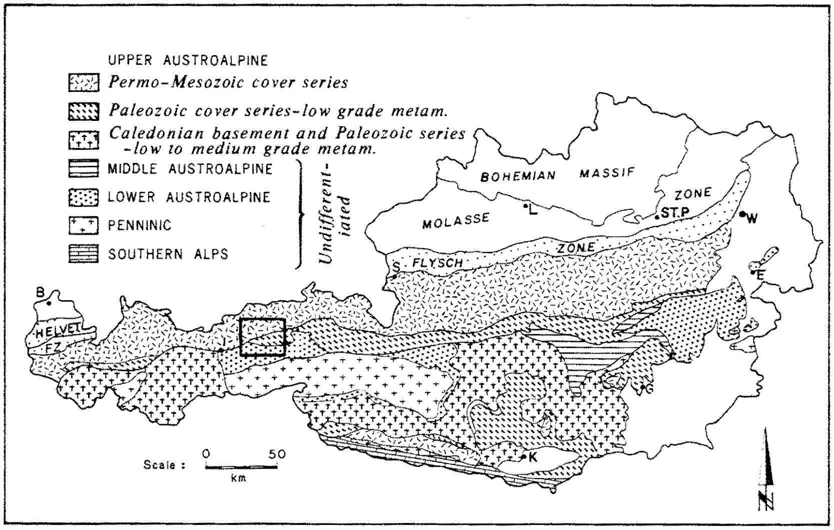

FIG. 1. Tectonic map of Austria (simplified after Frank, 1987) with the area shown in Figure 2 (Brixlegg) outlined. B = Bregenz, E = Eisenstadt, G = Graz, K = Klagenfort, L = Linz, S = Salzburg, ST. T = St. Pölten, W = Vienna.

dated biostratigraphically as Lower Devonian (Emsian) by Pirkl (1961) and Haditsch and Mostler (1969). The dolomite complex, which attains a maximum thickness of about 800 m in the Großkogel area, is underlain by a metapelitic and metapsammitic series of probable Upper Ordovician to Silurian age (see Fig. 2) with some intercalated acidic and basic volcanic layers (Wildschönau schists).

TABLE 1. Stratigraphic Units in the Brixlegg Area

Partnach beds (Ladinian-Karnian)	Slate, shale
"Muschelkalk" (Anisian-Ladinian)	Dolomite
Reichenhall beds (Upper Skythian-Anisian)	Rauwacke, dolomite
Werfen beds (Skythian)	Sandstone, slate, evaporite intercalations
"Buntsandstein" (Permian)	Red sandstone, slate
Hochfilzen beds (Lower Permian)	Dolomite-breccia, conglomerate
Schwaz dolomite (Lower-Middle? Devonian)	Dolomite with dolomite-breccia and evaporite intercalations, basal quartzite
Upper Wildschönau schists	Metapelites
Lower Wildschönau schists (Upper Ordovician-Silurian ?)	Metapsammites, basic and acidic volcanic intercalations
Kellerjoch gneiss (Caledonian ?-Hercynian ?)	Orthogneiss
Lower Austroalpine unit Innsbruck quartz-phyllite (Upper Ordovician-Silurian ?)	

A granitic orthogneiss (Kellerjoch gneiss) of probable Caledonian age (Satir and Morteani, 1979) forms the basement of the post-Upper Ordovician cover series. Within this basement gneiss, prograde metamorphism of amphibolite facies led to complete Rb-Sr homogenization, which has been dated by Satir and Morteani as Hercynian (322 Ma). There is evidence for tectonic movement between basement and cover series. These authors assume that the Kellerjoch gneiss belongs to the Lower Austroalpine Innsbruck quartz-phyllite unit, but it may also be part of the Upper Austroalpine basement juxtaposed to the Wildschönau schists by Hercynian tectonics. Its actual tectonic position remains equivocal and needs further investigation.

The Schwaz dolomite is overlain by a post-Hercynian clastic transgressive series which comprises the

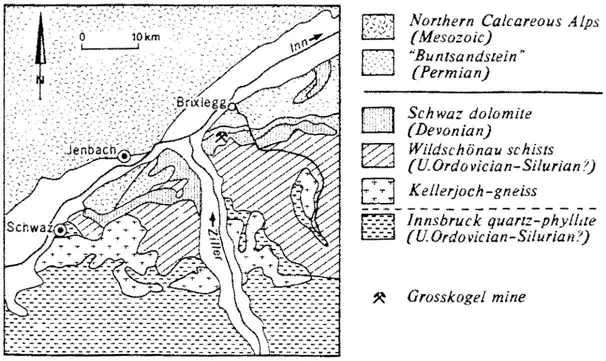

FIG. 2. Geologic map of the Brixlegg area, plus the location of the Großkogel mine.

Hochfilzen beds with reworked Schwaz dolomite components in their lower part, the Permian Buntsandstein and a Lower Triassic shallow-marine succession with evaporites and dolomites forming the base of the northern calcareous Alps. A detailed description of the various lithostratigraphic units and their regional distribution is given by Pirkl (1961). The stratigraphic units in the Brixlegg area are summarized in Table 1 (see also Fig. 2).

The early Paleozoic succession was affected by two orogenies, the Hercynian and the Alpine. The former caused folding and faulting under P-T conditions of lowest greenschist facies. Alpine tectonism caused thrusting of the Graywacke zone and the overlying northern calcareous Alps over Penninic and Lower Austroalpine units. Within the Schwaz dolomite intense block faulting is obvious.

Metamorphism

The rocks in the Western Graywacke zone were subjected to low-grade metamorphism. Illite crystallinity data (IC $< 0.25° \, 2\theta$) indicate epimetamorphic conditions (Kralik et al., 1987; Lengauer, 1988), the metamorphic grade generally decreasing toward the north. In the area around Brixlegg the epimetamorphic field reaches into the basal northern calcareous Alps. Metamorphism in the post-Hercynian transgressive series has been dated as Eoalpine (Kralik et al., 1987). The early Paleozoic rocks are, however, polymetamorphic. P-T conditions in these strata during the Hercynian and Eoalpine metamorphic events were on the order of 2 kbars and at least 300°C; celadonite contents in white mica, which have been determined by x-ray measurements, support somewhat higher pressures for the Hercynian metamorphism than for the Eoalpine (Lengauer, 1988). In the Schwaz dolomite complex quartz and dolomite remain stable together indicating that greenschist facies conditions have not been exceeded.

Distribution of Mineralization

The tunnels preserved from the old mine workings at the Großkogel mountain near Brixlegg allow an excellent three-dimensional insight into the various types of barite mineralizations in the Schwaz dolomite. The three levels, which were sampled along three north-south and one east-west profile, are shown in Figure 3. Although there is a certain local control on the barite distribution by tectonic features such as faults, the overall ore distribution seems to be quite random.

Most of the barite forms a very coarse grained monomineralic matrix of a monomictic breccia with embedded dolomite clasts. Locally, pipelike bodies of such breccia may reach dimensions of >100 m in length. Toward the margins of these brecciated ore pipes the dolomite becomes progressively cavernous. Cavities may have been filled previously by secondary anhydrite which was subsequently leached out. Often these mineralized dolomite breccias are restricted in their dimensions to barite dikes a few centimeters in thickness, with or without embedded dolomite.

Some of the barite occurs as stratiform layers. In these the barite forms very coarse grained fillings be-

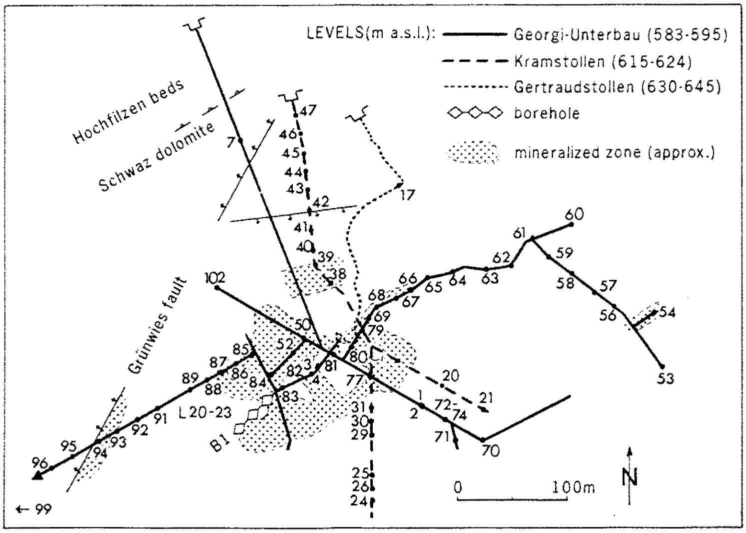

FIG. 3. Underground workings in the lower part of the Großkogel mine where samples were taken. Numbers refer to sample localities (prefix BK) of analyzed dolomitic host rock (see Table 3). The assumed outline of the major mineralized zones is indicated, as well as the location of borehole B1 (Table 3). Mineralization is confined to the Schwaz dolomite, which dips steeply to the northwest and is overlain by the Hochfilzen beds (see Table 1). m.a.s.l. = meters above sea level.

tween coarse-grained radial rhombic to bladed dolomite. No barite is associated with the anhydrite. In those horizons in which anhydrite is preserved, it occupies the remaining space between the rhombic to bladed dolomite.

Ag- and Hg-rich tetrahedrite occurs in varying proportions together with barite or with anhydrite. The general mineralization sequence is sparry dolomite → quartz + sulfide → barite or sparry dolomite → quartz + sulfide → anhydrite.

Apart from these types of mineralization, barite accumulations unassociated with signs of brecciation also exist. The youngest mineralization comprises barite veins into young fractures (barite II), tetrahedrite II, and anhydrite II. Carbonate remobilization into fractures as well as euhedral crystals of dolomite, calcite, and strontianite in drusy cavities is also seen.

In contrast to the neighboring mining areas at Schwaz, where barite is only a minor constituent or is totally absent, the dolomite in the barite-rich area at Großkogel appears coarsely recrystallized. The host rock, consisting mainly of fine-grained, bedded, dark gray or reddish, and in places, quartz-bearing dolomite I, is progressively replaced by a massive, coarse-grained white or light gray dolomite II. Barite mineralization is preferentially associated with dolomite II. In the field, a clear distinction between the two dolomite generations is often impeded by the occurrence of relatively medium-grained white dolomite I and restricted grain coarsening in impure dolomite II layers. Consequently, differentiation between various dolomite types fails to be a reliable indicator for the provenance of barite mineralization.

Chemistry of barite

Tufar (1964) determined Sr concentrations up to 4 wt percent in barites from the Großkogel area and considered this an indication of a hydrothermal origin. Microprobe and EDAX analyses also indicate a high variation in the Sr contents. On average, the barite I generation is more enriched in Sr than barite II, although no Sr phase could be detected within the barite crystals, either by means of XRD or electron microprobe analysis. This is in contrast to the observation of Leeder et al. (1983) who have shown that a high Sr content in similar hydrothermal vein barites is caused by minute celestite crystals intergrown with the barite. In the barites from Brixlegg, Sr seems to be incorporated into the lattice of barite and/or dissolved in fluid inclusions within the barite.

Analytical Techniques

For the Sr isotope study, largely silicate-free portions of unweathered dolomite and anhydrite samples were dissolved in 2.5 *N* HCl and centrifuged. In addition, some of the carbonate samples were analyzed as whole rocks. These were powdered and dissolved in 40 percent HF, concentrated HNO_3, and 6 *N* HCl after addition of a mixed Rb-Sr spike. The solution was evaporated to dryness and redissolved in 2.5 *N* HCl.

As pointed out previously, there is no evidence for any Sr-bearing phase within the barite that could have been formed before or after the barite itself. Therefore it can be assumed that the Sr in the barite originated from the same solutions as the barite. It did not seem necessary to dissolve the barite samples entirely by treating them with Na_2CO_3 and/or K_2CO_3, and they were prepared in the same way as the above-mentioned whole rocks but were not spiked. In this way up to 10 percent of the total Sr was extracted.

Rb and Sr were separated by conventional ion exchange techniques from the prepared solutions. Rb and Sr were individually loaded in 0.01 percent H_3PO_4 on tantalum single filaments. Measurements were performed on a VG MM30 solid-source mass spectrometer. All measured $^{87}Sr/^{86}Sr$ ratios were normalized to an $^{86}Sr/^{88}Sr$ ratio of 0.11940. The Sr isotope ratios listed in Tables 2 and 3 represent the average of 160 to 240 mass scans. Thirty-five analyses of the Sr standard NBS 987 during this study yielded a mean $^{87}Sr/^{86}Sr$ ratio of 0.70996 (±0.00008). This value seems to be relatively low compared to those reported from other laboratories but was obtained constantly on the instrument used over many years. The isotopic ratios of the analyzed samples were corrected to an $^{87}Sr/^{86}Sr$ ratio of 0.71014 for this standard. Analytical errors are expressed as 2 σ mean standard deviations. While the Sr and Rb concentrations in the dolomite samples were obtained by iso-

TABLE 2. Sr Isotope Ratios of Barite, Strontianite, and Evaporite Samples from the Brixlegg Deposit and Its Surroundings

Mineral	Sample no.	$^{87}Sr/^{86}Sr$	2σ mean (10^{-3})	Sr (wt %)
Barite I	BK6I	0.71303	0.08	2.40
Barite I	BK10	0.71313	0.08	0.95
Barite I	BK15	0.71280	0.09	0.43
Barite I	BK16	0.71281	0.11	n.d.
Barite I	BK52	0.71325	0.06	0.94
Barite I	BK99b	0.71307	0.10	n.d.
Barite I	BK111	0.71333	0.06	n.d.
Barite I	BK114	0.71284	0.05	0.68
Barite II	L20	0.71194	0.14	0.95
Barite II	L21	0.71214	0.17	2.10
Barite II	BK6II	0.71173	0.08	1.15
Barite II	BK96	0.71228	0.10	n.d.
Barite II	BK103	0.71215	0.09	0.43
Anhydrite	BK73	0.71080	0.06	0.19
Anhydrite	BK72	0.71065	0.07	n.d.
Gypsum	BK107	0.70910	0.08	n.d.
Strontianite	NHM	0.71263	0.17	n.d.

n.d. = not determined

TABLE 3. Sr, C, and O Isotope Data of the Dolomite Host Rock

Sample no.	Rock type	$^{87}Sr/^{86}Sr$	2σ mean (10^{-3})	$\delta^{13}C_{PDB}$ (‰)	$\delta^{18}O_{SMOW}$ (‰)	Sample no.	Rock type	$^{87}Sr/^{86}Sr$	2σ mean (10^{-3})	$\delta^{13}C_{PDB}$ (‰)	$\delta^{18}O_{SMOW}$ (‰)
L20	C	0.71187	0.20	0.80	22.06	BK62	B	0.70821	0.07	n.d.	n.d.
L21	B	0.71091	0.34	1.29	21.41	BK63	B	0.70850	0.08	2.13	26.58
L23	A	0.71093	0.16	−1.15	23.10	BK64	B	0.71271	0.06	0.91	23.45
BK1	A	0.70934	0.10	1.05	23.15	BK65	B	0.70860	0.06	n.d.	n.d.
BK2	A	0.71113	0.10	n.d.	n.d.	BK66	C	0.71289	0.35	n.d.	n.d.
BK3I	C	0.70945	0.05	n.d.	n.d.	BK67	C	0.70999	0.14	1.00	22.91
BK3II	C	0.71218	0.10	n.d.	n.d.	BK68	B	0.71144	0.28	n.d.	n.d.
BK4	B	0.71119	0.06	n.d.	n.d.	BK69	B	0.71134	0.22	n.d.	n.d.
BK7	C	0.70824	0.08	1.22	27.54	BK70	C	0.71244	0.43	0.90	22.16
BK17	C	0.71247	0.10	n.d.	n.d.	BK71	C	0.71207	0.23	n.d.	n.d.
BK20I	A	n.d.		0.67	22.09	BK73I	A	0.71222	0.18	n.d.	n.d.
BK20II	B	n.d.		0.85	21.31	BK73II	C	0.71253	0.17	1.14	21.18
BK21	C	0.71127	0.18	n.d.	n.d.	BK77	C	0.71234	0.73	n.d.	n.d.
BK24	A	0.71194	0.07	n.d.	n.d.	BK79	C	0.71158	0.22	0.79	21.99
BK25	B	0.71111	0.15	1.06	22.27	BK80	C	0.71108	0.49	1.23	23.98
BK26	C	0.71206	0.16	0.82	22.02	BK81	C	0.71005	0.15	0.97	22.54
BK29	C	0.70805	0.16	1.49	28.11	BK82	C	0.71248	0.21	0.93	21.72
BK30	A	0.71097	0.13	0.83	22.50	BK83	C	0.71125	0.29	1.10	21.75
BK31	C	0.70833	0.13	2.49	26.30	BK84	C	0.71054	0.07	n.d.	n.d.
BK38	C	0.71291	0.12	0.58	22.62	BK85	C	0.71191	0.21	n.d.	n.d.
BK39	B	0.71065	0.12	0.75	22.49	BK86	A	0.70989	0.27	n.d.	n.d.
BK40	A	0.71086	0.42	0.94	22.18	BK87	C	0.71145	0.17	0.36	21.95
BK41	B	0.70842	0.07	2.30	27.46	BK88	C	0.71230	0.15	n.d.	n.d.
BK42	B	0.71145	0.08	1.05	23.80	BK89	C	0.71071	0.07	0.96	21.47
BK43	A	0.70910	0.11	0.99	23.06	BK91	B	0.70763	0.09	1.94	24.19
BK44	B	0.71071	0.17	n.d.	n.d.	BK92	C	0.70810	0.07	2.09	27.47
BK45	B	0.71207	0.16	1.24	22.32	BK93	C	0.71184	0.11	1.12	20.89
BK46	B	0.71176	0.15	0.90	22.05	BK94	C	0.71213	0.50	0.70	20.98
BK47	A	0.71043	0.13	0.42	24.11	BK95	B	0.70821	0.10	2.06	25.80
BK50	B	0.70865	0.13	1.39	25.25	BK96	C	0.70879	0.06	n.d.	n.d.
BK52	C	0.70846	0.14	1.32	24.53	BK99b	C	0.71241	0.15	0.97	20.65
BK53	C	0.71212	0.18	0.70	21.85	BK102	C	0.71080	0.18	n.d.	n.d.
BK54	C	0.71179	0.21	n.d.	n.d.	BK109	A	0.70800	0.14	n.d.	n.d.
BK56	A	0.71166	0.13	0.93	21.83	BK110	C	0.71175	0.09	n.d.	n.d.
BK57	A	0.71331	0.87	−0.13	21.35	BK120	A	0.71041	0.11	n.d.	n.d.
BK58	C	0.71087	0.17	0.85	22.18	BK121	A	0.71217	0.12	0.62	22.23
BK59	C	0.71192	0.05	1.38	22.80	BK123	B	0.71010	0.07	n.d.	n.d.
BK60	B	0.70839	0.06	n.d.	n.d.	BK124	C	0.71010	0.13	n.d.	n.d.
BK61	B	0.70835	0.07	n.d.	n.d.	BK125	B	0.70816	0.15	3.06	28.05
Borehole B1 (dolomite)											
1.0–3.0		0.71132	0.13			14.0–14.5		0.71158	0.16		
3.0–3.5		0.71258	0.05			14.5–15.5		0.71168	0.11		
3.5–4.5		0.71233	0.11			15.5–16.0		0.71148	0.19		
4.5–5.0		0.71286	0.12			16.0–16.5		0.71086	0.54		
5.0–7.0		0.71258	0.07			16.5–17.0		0.71141	0.13		
9.5–10.5		0.71082	0.13			17.0–17.5		0.71109	0.09		
10.5–11.0		0.71219	0.11			32.5–34.0		0.71176	0.12		
11.0–11.5		0.71193	0.20			34.0–35.5		0.71148	0.09		
11.5–13.0		0.70914	0.44			35.5–36.0		0.71174	0.04		
13.0–13.5		0.71118	0.08			36.0–36.5		0.71100	0.12		
13.5–14.0		0.71011	0.52			36.5–37.0		0.71118	0.13		

For sample localities within the Grosskogel mine see Figure 3; BK109-BK125 are from surface outcrops in the vicinity of the mine
Rock types: A = fine grained, dark gray or reddish, B = coarse grained, dark gray, C = coarse grained, light gray
n.d. = not determined

tope dilution, the Sr concentration in barite was determined by EDAX and EMS.

For the C and O isotope analyses 50 mg of powdered sample were reacted under vacuum with 100 percent H_3PO_4 at 25°C for 24 hours. The liberated CO_2 was dried with a cooling mixture at −70°C and frozen into vessels by means of liquid nitrogen for mass spectrometric measurement. The same procedure was applied to the laboratory standard (Cararra marble).

Only two-thirds of the O present in the carbonate is transferred into CO_2 extracted from the rock. The ^{18}O values obtained were corrected for the different fractionation of calcite and dolomite according to Perry and Tan (1972). Measurements were performed on a VARIAN MAT 250 gas mass spectrometer.

In order to test whether eventual incomplete CO_2 yields would affect the results, sample BK 91 was treated for 24 and 48 hours. The difference in measured $\delta^{13}C$ and $\delta^{18}O$ was 0.03 and 0.04 per mil, respectively, which is within the instrumental error. The results of Table 3 are reproducible to ±0.1 per mil for C and O isotopes.

Sr Isotope Data

Most of the 117 samples investigated came from three different levels in the lower part of the Großkogel mine (see Fig. 3). A small number of samples was collected from various outcrops on the surface and from one borehole (see Fig. 3). Samples for isotope measurements came from an area about 2.0 × 1.5 km in size with level differences up to 600 m. This corresponds approximately to the extent of known barite occurrences. The main mineralized zone, as shown in Figure 3, seems to cover an area no greater than 100 × 200 m. Within this area $^{87}Sr/^{86}Sr$ ratios in the barite samples are relatively constant, 0.7117 to 0.7133 (see Table 2). This actually includes both barite generations. Separating barite I and II data, the isotopic composition of barite I is confined to values around 0.713, that of barite II to ratios around 0.712. No spatial dependence of the isotopic variation could be detected. Considering Sr concentrations between 0.4 and 4 percent and Rb concentrations below any detection limit, the isotopic ratios determined can be assumed as initial ratios corresponding to the isotopic ratio in the mineralizing fluid.

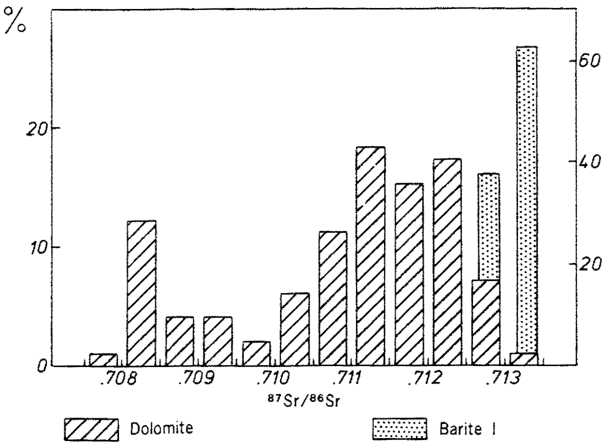

FIG. 4. Frequency distribution of $^{87}Sr/^{86}Sr$ ratios determined on 98 dolomite samples and eight samples of barite I from the Großkogel mine. The highest $^{87}Sr/^{86}Sr$ ratios in both dolomite and barite I are identical, indicating that dolomite recrystallization and barite precipitation was most likely caused by the same fluid. The lower frequency maximum in the dolomite population reflects the isotopic signature of contemporaneous seawater.

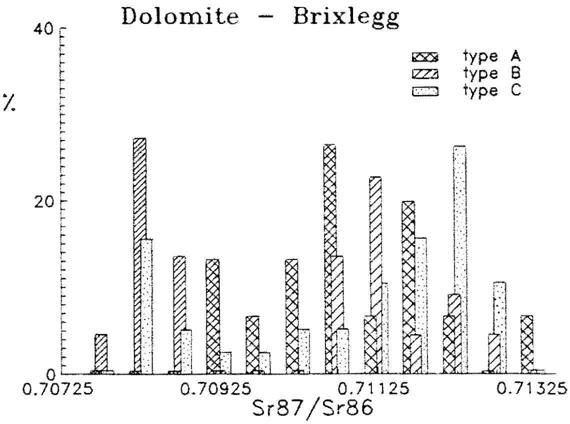

FIG. 5. Frequency distribution of $^{87}Sr/^{86}Sr$ ratios for the three dolomite types: A (fine grained, dark gray or reddish, bedded), B (coarse grained, dark gray), and C (coarse grained, light gray, massive). No clear difference exists in their $^{87}Sr/^{86}Sr$ ratios.

The $^{87}Sr/^{86}Sr$ ratios in the dolomite host rock ([Sr] = 30–40 ppm) vary between 0.7076 and 0.7133 (see Fig. 4). On a small scale (hand specimen), an increase in the Sr isotope ratio is obvious with the progressive recrystallization causing grain-coarsening. On a large scale, however, no dependence of the isotopic ratios upon grain size or other textural features is evident. Classifying the dolomite into three types, a fine-grained dark gray or reddish one, a coarse-grained dark gray and a coarse-grained light gray one, no systematic dependence between isotopic ratios and these types can be deduced from Figure 5.

The lowest ratios, which form a frequency maximum at 0.708 (Fig. 4), are in good accordance with contemporaneous Emsian to Middle Devonian seawater (Burke et al., 1982). In these dolomites the initial isotopic ratios at the time of deposition are preserved despite considerable recrystallization. This reflects a generally very low content of Rb-bearing silicate phases in the dolomite complex and/or very limited interaction with such silicates or ambient pore fluids.

Comparison between whole-rock data and data obtained on carbonate leachates shows that the higher Sr isotope ratios cannot be explained merely by in situ growth of ^{87}Sr. The Rb/Sr ratio is too low (<0.03) to alter significantly the initial isotopic ratio at the time of crystallization. This may be illustrated in the example of the dolomite with the highest Rb content measured (L23): [Rb] = 1.0 ppm, [Sr] = 35.5 ppm, $^{87}Rb/^{86}Sr = 0.084$. Although the $^{87}Sr/^{86}Sr$ ratio of the leachate is 0.71093 (Table 3), that of the whole rock is increased only to 0.71131. This means that dolomite recrystallization took place in the presence of fluids enriched in radiogenic Sr. Because the highest isotopic ratios determined in the dolomite are in perfect accordance with those of barite I, and these high ratios are only found in dolomite within or close to mineralized zones, dolomite recrystallization and barite mineralization can be attributed to the same fluids.

Anhydrite-forming relics of evaporitic horizons within the Schwaz dolomite yielded $^{87}Sr/^{86}Sr$ ratios of 0.71065 ± 0.00007 and 0.71080 ± 0.00006, respectively (Sr_{total} = 0.2 wt %). On a gypsum layer in the overlying Lower Triassic Werfen beds at the base of the northern calcareous Alps (sample BK107), an $^{87}Sr/^{86}Sr$ ratio of 0.70910 ± 0.00008 was determined.

Youngest sparry calcite mineralization filling drusy cavities within dolomite II has an Sr isotope ratio of 0.71728 ± 0.00008 which contrasts to its dolomitic surrounding (about 0.7123). Radial-fibrous bundles of strontianite on barite yielded an $^{87}Sr/^{86}Sr$ ratio of 0.71263 ± 0.00017.

Stable Isotope Data

Stable isotope data determined on 48 dolomite host-rock samples reflect a variation similar to that of the Sr isotopes (Table 3): the $\delta^{13}C_{PDB}$ values vary between −1.15 and 3.06 per mil and the $\delta^{18}O_{V\text{-}SMOW}$ values vary between 20.65 and 28.11 per mil. The frequency distribution of the $\delta^{13}C_{PDB}$ values shows a well-defined maximum at 1.00 per mil whereas that of the $\delta^{18}O_{V\text{-}SMOW}$ values exhibits an equally well defined maximum in the range between 22 and 23 per mil (see Figs. 6 and 7).

As with Sr isotopes, no distinct correlation between certain dolomite types and stable isotope variation can be established on a large scale. On a small scale, however, younger generations of recrystallized dolomite tend toward lighter O values. In the C isotope distribution, however, this trend to lighter isotopes is not so obvious.

In the youngest mineralizations forming late fillings in drusy cavities and fractures (calcite and strontianite, respectively) a distinct trend toward lower $\delta^{13}C_{PDB}$ values is evident (−3.53 and −4.07‰, respectively). The corresponding $\delta^{18}O_{V\text{-}SMOW}$ values are 25.02 and 17.18 per mil (uncorrected value, fractionation unknown), respectively.

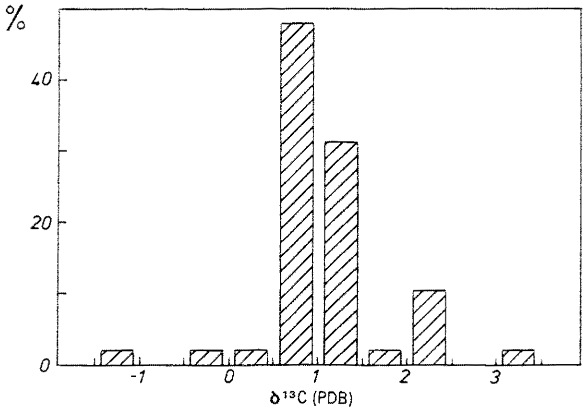

FIG. 6. Frequency distribution of $\delta^{13}C$ values of 48 dolomite samples from the Großkogel mine.

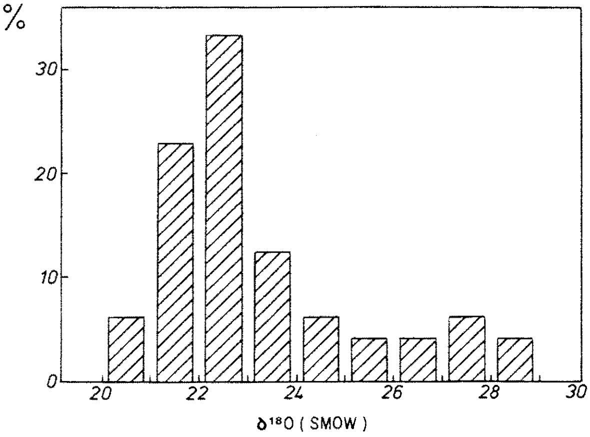

FIG. 7. Frequency distribution of $\delta^{18}O$ values of 48 dolomite samples from the Großkogel mine.

Correlation between Sr and Stable Isotope Data

Those dolomite samples which remained unaltered with respect to their Sr isotope composition (corresponding to contemporaneous seawater) are characterized by the highest $\delta^{13}C$ and $\delta^{18}O$ values; with $\delta^{13}C_{PDB}$ values of 1.5 to 3.0 per mil and $\delta^{18}O_{V\text{-}SMOW}$ values of 24 to 28 per mil, they are within the range of normal carbonate rocks (Keith and Weber, 1964).

A similar isotopic alteration with respect to C and O is evident (Figs. 8 and 9) in all dolomite recrystallizations which have been caused by the mineralizing fluids and which became isotopically altered with respect to Sr (increase in $^{87}Sr/^{86}Sr$ up to 0.7133). Both C and O isotopes were shifted toward lower values with increasing $^{87}Sr/^{86}Sr$ ratios. The difference in the $\delta^{13}C$ values is on the order of only 1.0, that in the $\delta^{18}O$ values of 4.0 per mil.

Comparison between the various frequency distributions in Figures 4, 6, and 7 shows that most of the dolomite samples investigated are altered isotopically with respect to the stable isotopes, giving one very distinct frequency maximum, whereas initial Sr isotope ratios are preserved in more of these samples giving two frequency maxima and a more gradual shift from unaltered isotopic ratios to ratios which can be considered typical for the mineralizing fluid.

Genesis of Barite

The Sr isotope composition of barites from Brixlegg is distinctly different from that of syngenetic barites from the Paleozoic of Graz (unpub. data, Frimmel, 1985). These Ba-Pb-Zn mineralizations, for which a

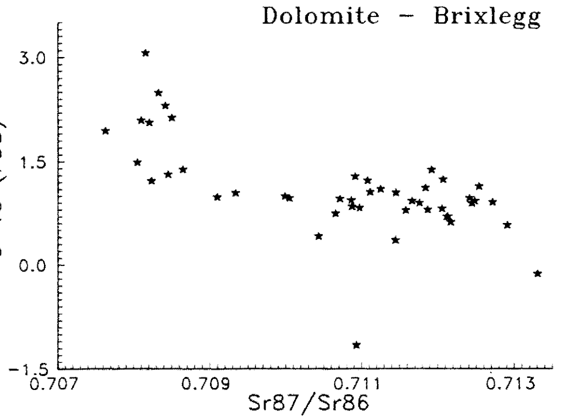

FIG. 8. $^{87}Sr/^{86}Sr$ vs. $\delta^{13}C$ diagram for Schwaz dolomite from the Großkogel mine showing a trend toward lower $\delta^{13}C$ values in samples which were altered isotopically due to interaction with the barite-precipitating fluid (compare Fig. 4).

synsedimentary volcanogenic exhalative model is well established, are bound to volcaniclastic strata of similar age as that of the Schwaz dolomite. The barites have a very constant isotopic composition ($^{87}Sr/^{86}Sr$ = 0.7079) which is in accordance with that of a greenschist layer nearby (0.7078), as well as with contemporaneous seawater.

The distinct difference between the isotopic ratios of barite, reflecting the isotopic composition of the mineralizing fluid, and the initial Sr composition of the Schwaz dolomite, corresponding to seawater, strongly supports an epigenetic origin for the barite. While structural evidence supports a syngenetic model for the tetrahedrite mineralization in the adjoining mining area around Schwaz (Gstrein, 1979), barite, which is only a minor constituent in the latter area but is concentrated in the Brixlegg area, should not be considered as a contemporaneous gangue mineral of the tetrahedrite. It has obviously been derived from another source and was introduced into the dolomite complex after its lithification. During this process, but at an earlier stage than the barite deposition, the dolomite recrystallized and the already existing sulfides were remobilized. A barite-free fine-grained tetrahedrite mineralization disseminated together with quartz along the very steep northwest-dipping bedding at the western margin of the Georgi-Unterbau level at the Großkogel mine, was considered by Schulz (1972) as evidence for a synsedimentary genesis. Actually, the dolomite in this stratiform orebody (BK57) yielded the most altered Sr isotope ratio (0.7133), thus emphasizing that this zone represents an epigenetic feeding channel rather than a synsedimentary mineralization.

The formation of barite is attributed to the reaction of Ba-rich solutions with anhydrite-rich evaporitic horizons within the Schwaz dolomite complex. Mossman and Brown (1986) have already pointed out that on thermodynamic grounds the conditions for extensive replacement of anhydrite are met in many subsurface formation waters.

The Sr may have been derived from the same source as the Ba and not from the evaporites and was probably introduced into the Schwaz dolomite by the same Ba-bearing solutions. Thus a marine signature of the sulfur in the $BaSO_4$ determined by Schroll and Pak (1980), the obviously nonmarine Sr in the barite, and the isotopic alteration of the dolomite in the vicinity of barite can be explained. At the margin of the percolated zone some anhydrite relics survived, presumably due to slight changes in the physical conditions of the fluid, but they experienced an Sr isotope alteration.

Relating the traces of Rb in dolomite sample L23 to authigenic sheet silicates, its Rb-Sr isotope data indicate an isotopic homogenization at 318 Ma. Although this figure is subject to a very big deviation, it supports a Late Hercynian age of the dolomite II and consequently also of the barite mineralization. Most of the anhydrite, which did not react to form barite at the first stage, was mobilized and dissolved later to a far-reaching extent, leaving behind numerous cavities within the dolomite.

Type and Source of Mineralizing Fluid

The isotopic data obtained place some constraints on the possible type of fluid causing the barite mineralization and Ag-Cu sulfide remobilization. Of the various types of metal-transporting waters, the only ones which could be characterized by $^{87}Sr/^{86}Sr$ ratios on the order of 0.713 are either meteoric, certain magmatic, or metamorphic waters.

Meteoric waters typically have $\delta^{18}O$ values less than 0 per mil. The dolomite should exhibit a more distinct

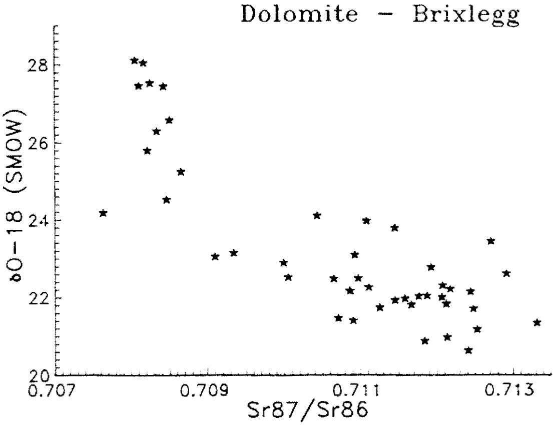

FIG. 9. $^{87}Sr/^{86}Sr$ vs. $\delta^{18}O$ diagram for Schwaz dolomite from the Großkogel mine. Comparison with Figure 4 shows a significant depletion in ^{18}O with increasing interaction between the dolomitic host and the fluid-precipitating barite.

shift to lower $\delta^{18}O$ values than is observed, if it had recrystallized solely in the presence of fluids derived from meteoric waters. Sr in meteoric waters at the time of karstification of the vast carbonate platform should be derived mainly from the dissolved carbonates, and therefore, should have an isotopic signature close to that in the dolomite approximating to seawater values. Younger meteoric waters could have reacted with evaporites at the base of the overlying northern calcareous Alps, thus providing a possible Sr source. These evaporites have a different Sr isotope composition (0.709), however.

Magmatic waters can be excluded from further consideration on the grounds that they generally have $^{87}Sr/^{86}Sr$ ratios much lower than 0.713, except waters derived from an S-type granitoid magmatism with considerable crustal contamination. There is no evidence for any such intrusion younger than Early Devonian in the Western Graywacke zone and its adjoining tectonic units.

An $^{87}Sr/^{86}Sr$ ratio of 0.713 would be in good accordance with regional metamorphic fluids enriched in radiogenic Sr due to interaction with Rb-bearing strata as, for instance, the metapelites and metapsammites underlying the Schwaz dolomite (Wildschönau schists). The isotopic ratios determined are evidence for metamorphic fluids being a major component of the ore-forming solutions. A certain input by meteoric waters cannot be excluded, however. Thus it seems that a mixture of metamorphic, meteoric, and diagenetically modified seawater, as to be expected in formation waters or orogenic brines, was the most probable metal-transporting medium.

If one assumes Sr concentrations in the mineralizing fluid of between 50 and 200 mg/l, on the basis of the Sr content and the Sr isotope shifts determined in the dolomite host rock and in the barite, minimum fluid/rock volume ratios between 1.5 and 3.0: 1 can be calculated for an open-system behavior. Such amounts of fluid can be generated most easily by the first metamorphism of a wet sediment pile. This is another argument for a Hercynian age of the mineralization.

The Schwaz dolomite I is more enriched in heavier C and O isotopes than contemporaneous and low-grade metamorphosed platform carbonates in the Eastern Graywacke zone ($\delta^{13}C_{PDB}$ = −0.7‰, $\delta^{18}O_{V\text{-}SMOW}$ = 20.0‰; Schroll et al., 1986) and probably contemporaneous marbles in the medium-grade metamorphosed crystalline basement at Hüttenberg ($\delta^{13}C_{PDB}$ = −0.5‰, $\delta^{18}O_{V\text{-}SMOW}$ = 19.4‰). Its C isotopie signature is similar to that of nonmetamorphosed Triassic limestones of the Upper Austroalpine unit ($\delta^{13}C_{PDB}$ between 2.2 and 3.7‰), but its O is even heavier than the O in the latter ($\delta^{18}O_{V\text{-}SMOW}$ between 24.5 and 23.5‰). Crystallization of dolomite I probably occurred at the peak of the first metamorphic overprint. As with the Sr isotope data, the C and O isotopes emphasize a relatively closed system during this process.

The subsequent recrystallization of dolomite in consequence of the activity of the mineralizing fluids caused a distinct shift toward slightly lower $\delta^{13}C$ and considerable lower $\delta^{18}O$ values (Figs. 8 and 9). This shift clearly shows that the mineralizing fluids must have been derived from an external source. It strongly supports an open-system behavior of the Schwaz dolomite during recrystallization. The observed C and O isotope shifts could be explained by two different fluid systems:

1. CO_2-rich fluids were liberated from carbonates in deeper crustal levels undergoing medium-grade metamorphism which had premetamorphic $\delta^{13}C_{PDB}$ and $\delta^{18}O_{V\text{-}SMOW}$ values around 0.0 and 22 per mil, respectively. Such CO_2-rich fluids would had to have been channeled through the metapelitic strata without significant reaction with graphite, implying very low fluid/rock ratios in the metaclastic series underlying the Schwaz dolomite.
2. CH_4-H_2O-rich fluids were expelled from the underlying metapelitic and metapsammitic series which underwent only low-grade metamorphism.

Geologic evidence exists for the latter possibility but not the former, because no major carbonate complexes are known anywhere under the Schwaz dolomite. The Schwaz dolomite itself never reached the P-T conditions which are necessary for the release of CO_2. Considering the lithologies of the basal Graywacke zone and its Hercynian basement, a CH_4-bearing H_2O-rich fluid seems most probable. Thus the source for the Ba and Sr that accumulated in the Schwaz dolomite can reasonably be assumed to be in the underlying series of the Wildschönau schists and metavolcanic intercalations therein, or from deeper tectonic units.

Economic Application

Ba-rich mineralizing fluids caused isotopic alteration halos in the Schwaz dolomite on the order of several tens of meters around the ore mineralizations. Until now lithologic and other geochemical data were not sufficient for the unequivocal identification of such altered dolomite. Sr isotopes appear to be an effective indicator of additional orebodies. The isotopic alteration halos are not regularly shaped but reflect different permeabilities in the dolomite host, thus the degree of alteration is no absolute measure for the distance from an eventual barite accumulation. It is, however, a valuable relative measure of the potential for mineralization of the dolomite. In a drilled dolomite core (see Table 3), for instance, the degree of isotopic alteration has given reliable information about the existence of mineralization in the vicinity of the borehole.

If one compares Figures 6 and 7 with Figure 4, it becomes obvious that in the case of the Schwaz dolomite the spread of the stable isotope data is not so marked as that of the Sr isotope ratios, thus making Sr isotopes more useful as a prospecting tool. This, however, depends upon the type of fluid-rock interaction and it may well be the other way around in other deposits.

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