

Mitt. Österr. Geol. Ges.	ISSN 0251-7493	86 (1993)	S. 141-152	Wien, August 1994
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Key words

*Eastern Alps
Metamorphic fluids
Metamorphogenic mineral deposits
Fluid inclusions
Light stable isotopes*

Alpidic Metamorphic Fluids and Metallogenesis in the Eastern Alps

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8 Text-Figures, 5 Tables

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Alpidisch-metamorphe Fluide und Metallogenese in den Ostalpen

Zusammenfassung

Schon früh in der geologischen Erforschung der Lagerstätten in den Ostalpen wurde vermutet, daß manche davon in Zusammenhang mit Gebirgsbildung und Metamorphose entstanden seien.

Mittlerweile gibt es zwei Modelle für die Bildung hydrothormaler Fluide durch Metamorphose. Das eine beschreibt die Bildung der Fluide durch Devolatilisierung bei der prograden Metamorphose, das andere bezieht sich auf große Konvektionssysteme von absinkenden Oberflächenwässern während der retrograden Abkühlungsphase metamorpher Komplexe.

Eine eindeutige Zuordnung einzelner Lagerstätten zur metamorphogenen Klasse ist auch heute noch sehr schwierig; deshalb wurde hier ein regional vergleichender Ansatz gewählt, da metamorphe Fluide auf Grund ihrer Äquibrierung mit großen Gesteinsmassen über weite Bereiche ähnliche Eigenschaften aufweisen sollten. Die Untersuchung von Fluideinschlüssen und zugehörigen Systemen leichter, stabiler Isotope in einer Auswahl möglicher metamorphogener Lagerstätten der Ostalpen bestätigt diesen Ansatz.

Jene Lagerstätten, die unmittelbar nach der kretazischen Metamorphose und Orogenese gebildet wurden (Mitterberg, Erzberg, Schendleck, Kleinkogel, Rabenwald), enthalten wässrige, hochsalinare Fluide, deren Wässer nach H- und O-Isotopendaten ins metamorphe Feld fallen. Da solche Fluide nur im Ostalpin gefunden wurden, können sie als Produkt der metamorphen Devolatilisierung von Gesteinen des subduzierten südpenninischen Troges aufgefaßt werden, die nach der Kollision des Ostalpins mit dem Briançonnais während einer Relaxationsphase nach oben abströmen konnten.

In deutlichem Gegensatz dazu wurden die nach der eozänen Orogenese entstandenen Lagerstätten (Hüttenberg, Waldenstein, Klienung, Gastein) durch Fluide mit hohem CO₂-Gehalten und niedriger bis mäßiger Salinität gebildet. Kohlenstoffisotopendaten deuten auf eine Ableitung des CO₂ aus dem Mantel, z.T. vielleicht auch aus metamorphen Fluiden der tiefliegenden penninischen Serien. Das Wasser der Fluideinschlüsse dieser Lagerstätten ist isotopisch sehr heterogen, was am ehesten durch Mischung von absinkenden Oberflächenwässern mit metamorphem Tiefenwasser erklärbar ist. Die tektonische Kontrolle dieser zweiten Gruppe von Lagerstätten sind Störungen der oligozänen und miozänen Scherungs- und Dehnungstektonik in den Ostalpen. Dadurch wurden einerseits von Oberflächenwasser gespeiste, tiefreichende hydrothermale Konvektionszellen gebildet, andererseits konnten tiefe, während der jungalpinen Metamorphose freigesetzte Fluide hochströmen. In den Aufstiegszonen der Hydrothermen sind die Lagerstätten entstanden.

Abstract

Fluid inclusions and stable isotope data concerning mineral deposits which were traditionally thought to be related to the two major orogenic phases of the Eastern Alps confirm this differentiation.

Deposits formed immediately after the first, Cretaceous orogeny, were produced by fluids of very high salinity and with an isotopic composition of the water falling into the metamorphic field. These fluids are best understood as products of metamorphic devolatilization of rocks of the subducted South Penninic domain.

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In contrast the deposits formed after the second, Tertiary orogeny, originated from fluids with an appreciable content of CO₂ and low to moderate salinities. Carbon isotopes indicate a deep crustal or even mantle source for CO₂ while water is isotopically more heterogeneous and may have mixed sources, both surficial and metamorphic. Tectonic control of these mineralizations is postorogenic transtensional faulting, which exposed hot metamorphic rocks to fluid convection along brittle structures. These deposits best conform to the model of metamorphogenic metallogenesis by retrograde leaching.

1. Introduction

A genetic relation between some mineral deposits of the Eastern Alps and regional metamorphism was tentatively discussed already by CLAR & FRIEDRICH (1933), but in spite of recurrent comparable considerations satisfactory conclusions could not be reached (PETRASCHECK, 1989).

Meanwhile, both the understanding of the evolution of this orogen and the general modelling of metamorphogenic mineralization (POHL 1992a) have progressed considerably, and several recent papers on various aspects of individual Alpine deposits have alluded to a possible metamorphic origin (e.g. FRIMMEL, 1988).

This article intends to present investigations with a regional and comparative emphasis rather than concentrating on genetic discussions of individual deposits. It is mainly based on microthermometric and stable isotope data of fluids which have formed mineral deposits in the Eastern Alps.

We selected those epigenetic deposits, which were either traditionally attributed an age coinciding with the main orogenic phases (Erzberg, Mitterberg, Rabenwald) or which were considered to be late to post-tectonic (Hüttenberg, Waldenstein, Gastein) (W. PETRASCHECK, 1947; CLAR, 1953; W.E. PETRASCHECK, 1947). Neither systematic fluid inclusions data nor light stable isotope compositions were available on these deposits until now, with the exception of a recent paper by PROCHASKA (1993), where oxygen and hydrogen isotopic compositions are reported for two of the deposits investigated here (Schendleck and Mitterberg).

Metamorphogenic mineral deposits are defined now to have formed from hydrothermal solutions, which are expelled from geological bodies undergoing active metamorphism (POHL, 1992). This may either be prograde, and then the fluids are the product of devolatilization, or the metamorphism may be retrograde, in which case the water involved can have various sources (marine, meteoric, etc.). In the first case, the equilibration of the fluid with the metamorphic rocks at very low water/rock ratios will be most complete, and it is therefore called metamorphic. In retrograde reactions, the fluids may retain some of their original properties, as full equilibration with metamorphic country rocks is often not reached because of higher and variable water/rock ratios.

In actual geological processes, these two models of fluid evolution most probably do not exclude each other. Accordingly, specific deposits may have been formed by mixing of ascending devolatilization fluids with convecting meteoric waters.

As very large crustal volumes are involved in prograde metamorphic processes, the metamorphic derivation of mineralizing fluids during orogenic cycles should result in a distinct grouping of at least some of their properties, even if local peculiarities are to be expected considering variable source rock mixtures, further reactions along flow paths, and changes at the site of mineralization. In the following, this working hypothesis of "fluid provinces" will be tested in its applicability to Alpidic mineralization in the Eastern Alps.

2. Geological Evolution and Metamorphism of the Eastern Alps

Similar to wide areas of Central and Western Europe, the Alpine region was affected by the Hercynian orogeny during the Late Paleozoic. Ending a complex evolution from the Late Proterozoic to the Lower Carboniferous, this left a variably metamorphosed and deformed basement to most of the subsequent Alpidic (*sensu stricto*) tectonic units (FRISCH & NEUBAUER, 1989). Mineral deposits formed in the area of the later Eastern Alps during the Pan-African and Hercynian cycles are not considered in this paper.

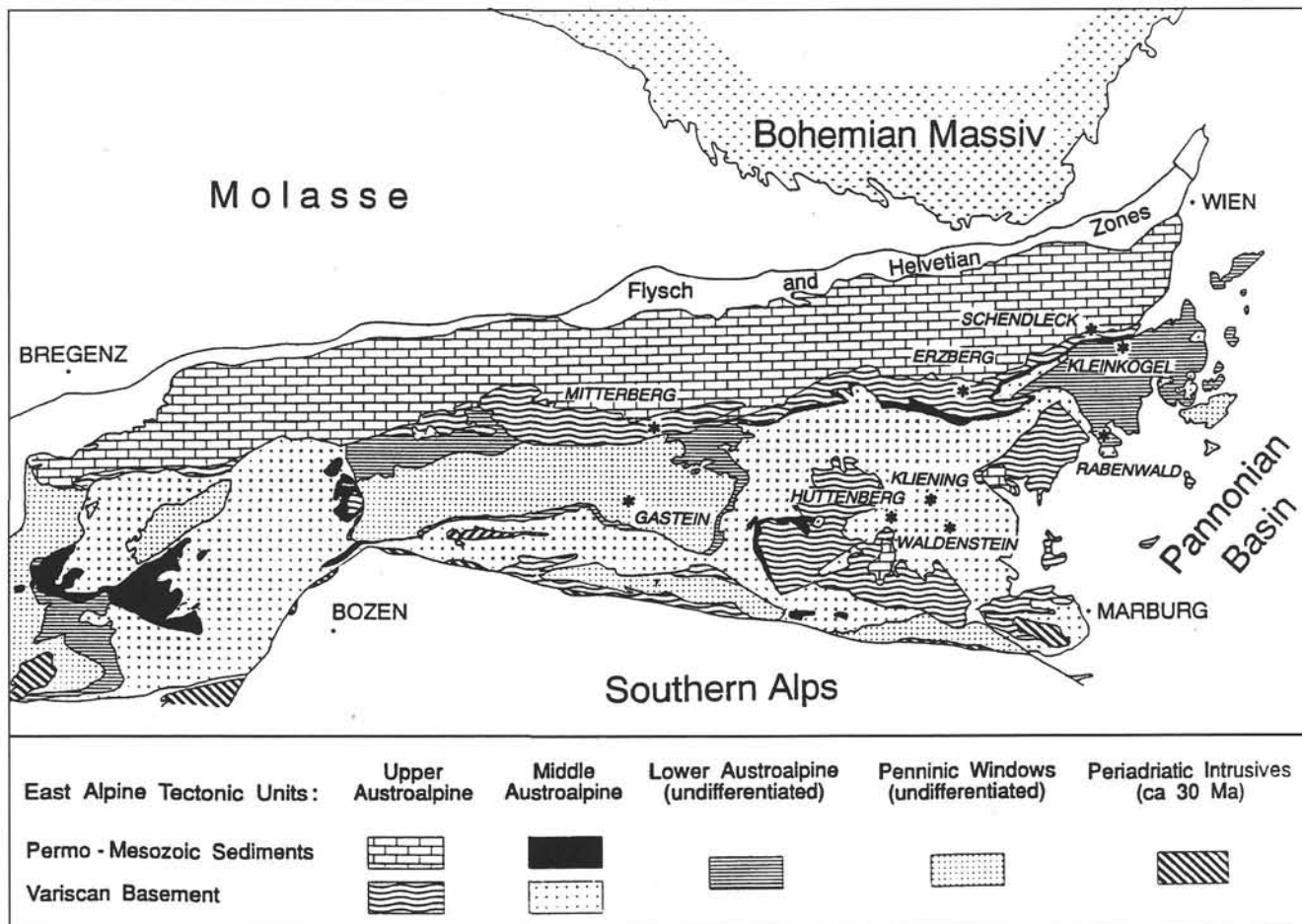
The Alpidic cycle started in the Permian. From the Permian to the uppermost Jurassic, the region of the Eastern Alps has been affected by several periods of extensional tectonics (Permian, Middle Triassic, Jurassic) which culminated in the formation of the Penninic ocean (FRISCH, 1981). During the same time span, wide areas were submerged below sea level which resulted in the accumulation of Permo-Mesozoic sediments partly reaching a thickness of several kilometers. In the Jurassic, a southern continental plate (comprising the Austroalpine-Southalpine and Dinaric zones of the Adriatic plate) developed a passive continental margin towards the South Penninic ocean.

During the Lower Cretaceous, the extensional stress regime turned into a compressive one, with southeastward subduction of the South Penninic oceanic plate underneath the Austroalpine ending at about 90 Ma (Turonian) followed by continental collision and southward subduction of the northern plate with a second orogenic climax in the uppermost Eocene (ca. 40 Ma). During this long orogenic period, sedimentary troughs were progressively shifted outwards from the center of the orogen, while the large thrust sheets often comprising basement as well as Mesozoic cover rocks advanced towards the West and North.

Thus, the Austroalpine plate was dissected into three major tectonic units, the Lower, Middle and the Upper Austroalpine, which were then superposed on each other (TOLLMANN, 1987). Each unit comprises many smaller basement and/or cover nappes.

In relation to the deformational phases, two main time spans of metamorphism could be distinguished in the Eastern Alps: an earlier, "eoalpine" phase during the Cretaceous, and a later "neoalpine" or "Tauernphase" in the Eocene-Oligocene (40–35 Ma: FRANK et al., 1987). The time of eoalpine metamorphism varies widely in different tectonic units and some dates near the turn Jurassic/Cretaceous reflect probably crustal thinning rather than orogenic metamorphism. The ophiolites and metasediments of the South Penninic ocean give K/Ar-ages for blueschist metamorphism overprinting previously formed eclogites between 90 to 60 Ma (FRANK et al., 1987). Eclogites in the Middle Austroalpine basement were formed at about 100 Ma and retrograded to amphibolite facies at 90 Ma (THÖNI & JAGOUTZ, 1992).

Accordingly, the peak of fluid activity during eoalpine metamorphism may conveniently be considered to have occurred at about 90 Ma (Turonian).



Text-Fig. 1. Tectonic units of the Eastern Alps (after TOLLMANN 1977) and location of mines and mineralizations of suspected metamorphogenic origin during the Alpidic cycle.

Soon after the second, Tertiary climax of orogeny and metamorphism at about 40 Ma, the thickened orogenic wedge of the Eastern Alps started to collapse. From about 30 Ma (Oligocene) onwards, conjugate shear zones and faults were formed resulting in extension towards the rapidly opening Pannonian basin in the East ("lateral extrusion" – RATSCHBACHER et al., 1991). This coincides with progressive cooling of the orogenic body, Probably to a considerable degree by convective fluid flow, involving mainly surface derived water.

3. The Investigated Mineral Deposits

A total of 10 mineral deposits of possible metamorphogenic origin during the Alpidic orogenic cycle were investigated for this study (Table 1). This selection tried to sample the major tectonic units of the Eastern Alps (Text-Fig. 1) as well as to include various mineralization types. Some of the localities represent active mines (Erzberg, Rabenwald, Waldenstein), while others are either exhausted or at present uneconomic. Most of the deposits have been mentioned by HOLZER (1986), where references to earlier, more detailed descriptions can be found.

The former copper mine at **Mitterberg** exploited a quartzcarbonate-chalcopyrite vein hosted by phyllitic country rocks of Lower Paleozoic, Upper Carboniferous and Permian age. The vein strikes E–W and has a steep southerly dip, crosscutting both Variscan and Alpidic schistosity. Its known extensions reach a length of about 11 km and a

Table 1. Attribution of the investigated deposits to the major tectonic units of the Eastern Alps, and main mineral/ore produced.

AUSTROALPINE	Upper	Mitterberg Erzberg Schendleck	chalcopyrite siderite siderite
	Middle	Hüttenberg Waldenstein Kliening	siderite hematite (specularite) Au
	Lower	Kleinkogel Rabenwald	baryte talc
PENNINIC		Schlainig*) Gastein	stibnite Au

*) Schlainig is not further considered here, as this deposit was confirmed to be related to Miocene andesitic volcanism of the Pannonian basin (BELOCKY et al., 1991).

depth of nearly 600 m. Uraninite found in the uppermost parts of the vein has been dated by the U–Pb method (90 Ma: PETRASCHECK, 1978).

The iron ore mine at **Erzberg** is well known in the European literature as the type deposit for hydrothermal-metasomatic siderite in marine platform carbonates (POHL,

1992b). Although this model met various contradictions (e.g. BERAN, 1979), it meets best both, earlier observations as well as our data. The deposit occurs in the Paleozoic basement of the Upper Austroalpine unit. A large magnetic anomaly nearby is thought to reflect the presence at depth of a big body of (Ordovician?) basic volcanic rocks (METZ et al., 1979). At Erzberg, Variscan thrusting caused repetition of a sequence of Lower Devonian limestones. This is transgressed by terrestrial red sediments of Permian age, which are the base of a thick marine suite of Mesozoic sediments. In the mine area, hydrothermal alteration and quartz-carbonate veining affect all rocks from the Ordovician in the footwall to the Permian in the hanging wall (SPINDLER, 1992). This imprint is clearly younger than the Alpidic schistosity and low grade metamorphism. Massive siderite forms irregularly shaped, although stratabound bodies in Lower Devonian limestones. Fine grained ankerite envelops many ore bodies (BERAN, 1979), this may be interpreted as a hydrothermal alteration halo, although elsewhere siderite and limestone are in direct contact. Ankerite-quartz-sulfide veinlets are ubiquitous near the margins of many ore bodies, cross-cutting both siderite and country rock. Analyzing Sr-isotope ratios of siderite and enclosing limestones, FRIMMEL (1988) found distinctly higher $^{87}\text{Sr}/^{86}\text{Sr}$ in siderite. Based on this fact he concluded, that the origin of the deposit was epigenetic.

Schendleck was a small iron ore mine. Siderite occurs here in a thick vein, partly massive, partly as matrix of a country rock breccia. The latter is an Ordovician, low grade metamorphic quartz porphyry (Blasseneck-Porphyröid). Quartz and traces of sulfides developed near the vein contacts and in a stockwork zone in the footwall. The veins are clearly discordant to Alpidic schistosity, and hydrothermal alteration of the porphyry is distinct (e.g. sericitization).

Much larger than Schendleck, although second to the Erzberg with respect to its ore reserves was the former siderite mine of **Hüttenberg**. Country rocks of the ore bodies are members of a multiply deformed and metamorphosed volcano-sedimentary suite of supposedly Lower Paleozoic age, comprising paragneisses, schists, amphibolites, Variscan pegmatites, and marbles. Eclogites in the immediate neighbourhood suffered high pressure metamorphism at about 100 Ma, and retrograding to amphibolite facies at about 90 Ma (THÖNI & JAGOUTZ, 1992). Sideritization of the marbles, however, is distinctly younger, as country rocks are sericitized or chloritized, and the ore is drusy and contains numerous, small idiomorphic quartz crystals. Druses and veins cutting the ore contain quartz, baryte and carbonates with minor amounts of sulfides (Fe, Pb, Zn, Cu, As, etc.). Similar to Waldenstein (see below), formation of the deposit was related to one of the major transtensional faults affecting the Eastern Alps in the Oligocene-Miocene (CLAR & MEIXNER, 1981).

Waldenstein is a much smaller accumulation of iron compared to Hüttenberg, but the specularitic nature of its hematite ore which can be used for the production of anti-corrosive fillers makes it a highly economic, small mining operation. The country rocks are nearly identical to those of Hüttenberg, and here also marbles are replaced by the ore, which forms irregular pipes and stocks, apart from numerous small veinlets. Economic ore consists of nearly monomineralic, soft hematite rock, formed by delicate, platy aggregates and rosettes of specularite. In addition, there occur idiomorphic pyrite crystals, some magnetite and graphite in the ore, and calcite and quartz in druses and veinlets. Country rock alteration includes sericitization, carbonatization and chloritization. Marbles adjoining ore bodies are coarsely recrystallized. Tectonic control is brittle faulting

related to a large transtensional fault of Tertiary age passing near the deposit. Based on geochemical and isotope data, PROCHASKA et al. (in print) confirm a hydrothermal origin of the deposit.

The same fault system controlled the formation of the quartzcarbonate veins of the former gold mine at **Kleining**. The gold was either native or associated with arsenopyrite, pyrrhotite and pyrite. In addition, traces of various sulfides (Bi, Cu, Co, Pb, Zn) and arsenides have been found.

Kleinkogel was a small baryte mine exploiting a short but thick vein deposit hosted by Triassic quartzite of the Lower Austroalpine unit. The vein is clearly fault-bound and epigenetic. Baryte is partly intergrown with quartz, especially in smaller veinlets which occur in the footwall off the deposit. From field evidence it may be concluded, that the emplacement of mineralization is younger than the Alpidic metamorphism of the quartzite.

The large talc mine at Rabenwald is situated in the gneissic basement of the Lower Austroalpine unit. Here, a suite of paragneisses and schists was thrust cover coarse grained orthogneiss during the Cretaceous orogeny. The thrustplane contains remnant blocks of magnesite, which are surrounded by talc and chlorite ore. According to geochemical relations, the talc appears to be derived from magnesite (PROCHASKA, 1989). Gneisses near the talc ore are altered to quartz-phengite-chlorite (kyanite) rocks which indicate high P/T conditions during one stage of the evolution of the thrust plane (500–550°C/8–9 kbar: MOINE et al., 1989).

The former gold mine south of **Gastein** was exploiting several left-lateral, brittle shear zones of north-northeasterly strike which crosscut the alpidic foliation of Variscan granites and of overlying nappes of meta-sediments in the Tauern window of the Penninic Zone (FEITZINGER & PAAR, 1991). In this area, metamorphic conditions during the Eocene reached 400–500°C and 4–6 kbar (FRANK et al., 1987). Cooling (K-Ar) ages of white micas in the Penninic spread from 30 to 10 Ma, depending on the structural level. The shear zones contain patches of quartz and carbonate which carry gold associated with arsenopyrite and pyrite. Small amounts of other sulfides and sulfosalts (Pb, Zn, Cu), and of tetrahedrite are present. Macroscopically visible hydrothermal alteration of the country rocks includes silicification and sericitization.

4. Fluid Inclusion Studies

4.1. Microthermometry

Current heating and freezing microthermometric methods (SHEPHERD et al., 1985) were employed using a LINKAM THM 600-TMS 90 stage. Data determined for individual inclusions comprised $T_M\text{CO}_2$, (semiquantitative determination of N_2 and CH_4), T_{EM} (eutectic melting indicating cations other than Na), T_M hydrohalite (for Na/Ca ratios), T_M ice (to obtain wt % NaCl equivalent), and T_M clathrate (salinity of CO_2 -rich inclusions). Heating runs were made for measurements of $T_H\text{CO}_2$ (to estimate density of CO_2 phase), $T_S\text{NaCl}$ (for concentration of oversaturated solutions), T_H (total homogenization into vapor or liquid phase), and in some cases T_D (decrepitation when this occurred before homogenization).

Wherever possible, inclusions in hydrothermal quartz were investigated in order to avoid problems typical for less stable minerals. Only in some cases, where not enough

Table 2. Main compositional data and homogenization temperatures (T_H) of fluid inclusions in quartz from investigated deposits of Cretaceous age.

Location	Inclusion type	wt% NaCl equiv.	T_H °C	D (g/cm ³)	Composition (wt %)
<i>Mitterberg</i>	MIT 1a	26-38	127+38	1,15-1,22	H ₂ O, halite, (calcite)
	MIT 1b	c.23	c.100	1,1	H ₂ O
<i>Erzberg</i>	ERZ 1a	c.23	110-140	1,1 NaCl	H ₂ O, + CaCl ₂ !
	ERZ 1b	13-15	c.150	c.1,0	H ₂ O
<i>Schendleck</i>	SCH 1a	22±0,5	50-100	1,11-1,14	H ₂ O
	SCH 1b	29-31	80-90	c.1,19	H ₂ O halite, NaCl+ CaCl ₂
<i>Kleinkogel</i>	KLE 1a	31±2	110-140	1,16-1,2	H ₂ O halite
	KLE 1b	17±4	130±20	1,03-1,09	H ₂ O
<i>Rabenwald</i>	RAB 1	25-65	117±16	1,22-1,25	H ₂ O halite
	RAB 2a	26±0,4	130±11	c.1,15	H ₂ O halite
	RAB 2b	c.19	125±6	c.1,09	H ₂ O

quartz was available, inclusions in carbonates were used and compared with those in rare quartz specimen. An extensive description of the samples, of methods employed, of the results of measurements and of their interpretation was given by BELOCKY (1992). Here, we report these results in a condensed form:

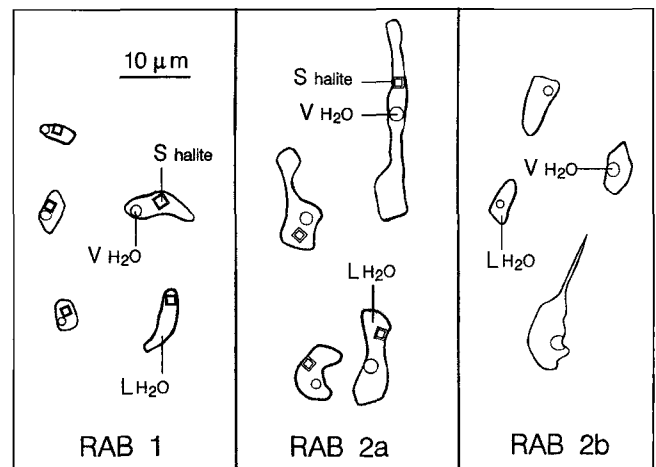
At Mitterberg, quartz was sampled from the least deformed

third mineralization phase, whose paragenesis consists of chalcopyrite, pyrite, arsenopyrite, galena, tetrahedrite, ankerite and quartz (BERNHARD, 1966). The quartz contains primary inclusions (MIT 1) which are irregularly dispersed, and inclusions arranged along later secondary planes (MIT 2). Among the first group, a further subdivision is possible into a subgroup with daughter crystals of halite and rarely calcite or ankerite (MIT 1a), and a second subgroup without solid phases (MIT 1b). Both have very high filling rates approaching 100 %, i.e. vapour bubbles are very small or absent. In the latter case, vapour bubbles formed during melting after freezing the inclusion. The densities of MIT 1 inclusions are high and homogenization temperatures are low (Table 2). Upon further heating, dissolution of the halites of MIT 1a occurs at 240°C and at a pressure of about 2 kbars. Because of kinetic reasons, the carbonates cannot be dissolved. T_S halite therefore constrains the minimum trapping conditions of these fluids. TFM at between -40 to -50°C points to an elevated content of CaCl₂. MIT 2 fluids have much lower salinities. Overall, the fluid evolution at Mitterberg is relatively simple, starting with high salinities which diminish progressively in time.

Fluid inclusions in rock forming siderites at Erzberg are too small for microthermometric investigations. Therefore, quartz and siderite from ubiquitous small veinlets and druses in the ore were sampled. Both minerals contain ERZ 1a inclusions with about 23 wt % NaCl equivalent, with an important share of CaCl₂. Halite daughter crystals were not seen in the samples, although they were observed in similar inclusions from the genetically comparable siderite occurrence at the Leobener Hütte on the nearby Polster mountain. ERZ 1b inclusions with lower salinities occur in quartz only. Similar to Mitterberg, filling rates and fluid densities of the aqueous inclusions are elevated, while homogenization occurs at relatively low temperatures (Table 2). Optically, the vapour bubbles appear to consist of water vapour only. SPINDLER (1992), however, reports that they contain CO₂ besides water as shown by infrared spectroscopy. The isochores are quite steep (BELOCKY 1992), however, imply-

ing high trapping pressures at probable formation temperatures, i.e. 2,5 kbars at 250°C. The mineralizing fluids at Erzberg evolved from early saline to later more dilute compositions. The high CaCl₂ contents in early fluids reflect the metasomatic reaction between hydrothermal fluids with dissolved Fe²⁺ and the limestones, which must have liberated large amounts of Ca²⁺.

At Schendleck, fluid inclusions in quartz and siderite both from the main ore body and from cross-cutting veinlets were investigated. They are aqueous, saline, quite dense, and have filling rates near 100 %, which explains the very low homogenization temperatures (Table 2). Inclusions with halite daughter crystals and high salinities reaching 31 wt. % NaCl equivalent (SCH 1b) are rare. Most others contain about 22 wt. % NaCl equivalent (SCH 1a). The ratio of dissolved NaCl/CaCl₂ as estimated from melting of hydrohalite at -28°C is about 2. P/T conditions of trapping cannot be constrained. Calculation of the isochores of



Text-Fig. 2. Fluid inclusion types in quartz veinlets syngenetic with talc at Rabenwald, as an example for saline fluids of the syn-orogenic Austroalpine fluid province.

Table 3.
Main compositional data and homogenization temperatures (T_H) of fluid inclusions in quartz from investigated deposits of Tertiary age.

Location	Inclusion type	wt% NaCl equiv.	T_H °C	D (g/cm ³)	Composition (wt %)
Hüttenberg	HÜ 1a1	c.8	460-480	c.0,4	H ₂ O, c.55% CH ₄
	HÜ 1a2		320-360		CO ₂ , CH ₄ , H ₂ O
	HÜ 1b		c.355		H ₂ O, CH ₄ , CO ₂
	HÜ 2	18-22	210-260	0,96-1,04	H ₂ O
	HÜ 3a	8,5±0,6	326±10	c.0,91	H ₂ O, 32-38% CO ₂
	HÜ 3b	8,6±0,4	284±13	c.0,93	H ₂ O, 23-26% CO ₂
	HÜ 4a	31,5±2	300-340	c.1,0	H ₂ O, halite, calcite, ?mirabilite
	Hü 4b HÜ 5	23±1 n.d.	315-340 T_D+300	c.0,92 n.d.	H ₂ O CO ₂ +CH ₄ , H ₂ O
Waldenstein	WAL 1a	24±1	135-260	1,0-1,1	H ₂ O, NaCl + CaCl ₂
	WAL 1b	27-34	130-200	c.1,14	H ₂ O, halite, calcite
	WAL 2	5-22	300-400	n. d.	CO ₂ , H ₂ O
Kliening	KLI 1	7,4±0,7	188±20	c.0,93	H ₂ O
	KLI 2a	2-4	n.d.	n.d.	H ₂ O, CO ₂
	KLI 2b	n.d.	n.d.	n.d.	CO ₂ , H ₂ O
Gastein	GAS 1a1	6,2±1,6	390±32	0,5-0,6	55-75% CO ₂ , H ₂ O
	GAS 1a2	6-7	320±10	0,8	H ₂ O, 15-25% CO ₂
	GAS 1b	6-7	300±10	0,8	H ₂ O, < 5% CO ₂
	GAS 2	2-3	153±28	0,9-0,94	H ₂ O

SCH 1a (BELOCKY, 1992), however, shows that at a presumed trapping temperature of 250°C the corresponding pressure would be 3,5 kbars.

Quartz samples were investigated from the baryte-quartz veins at Kleinkogel, as the baryte is too fine grained for microthermometric analysis. Pseudosecondary inclusions arranged in planes comprise a subgroup with halite daughter crystals (KLE 1a), and a second without a solid phase (KLE 1b). Both have high filling rates, elevated densities, and low homogenization temperatures. Halite dissolution occurs at 150–200°C, which represents the minimum trapping temperature. This implies formation at or above a pressure of 1,5 kbars. The high K-content of the fluids (Table 4) confirms earlier suggestions that albitization of potassium feldspars of the underlying Variscan granite gneisses may have provided the Ba to the rising hydrothermal fluids.

The talc deposit at Rabenwald was probably formed by hydrothermal SiO₂-rich solutions which reacted with preexisting magnesite (PROCHASKA, 1989). Therefore, samples of quartz veinlets and pockets in talc and its immediate country rocks were used for this study. Three fluid inclusion types were recognized (Text-Fig. 2): RAB 1 are primary and contain halite daughter crystals, RAB 2a have also solid halite

but occur in pseudo-secondary planes, and RAB 2b are saline but without halite and occupy secondary microfractures. All inclusions have high filling rates, low homogenization temperatures, and densities above 1 (Table 2). T_S halite of RAB 1 inclusions ranges from 250 to >350° C. Those approaching the high temperatures, however, decrepitate upon heating before halite is dissolved. This, and the wide salinity range of RAB 1 inclusions may indicate accidental trapping of halite crystals. T_{FM} of all inclusions is extremely low (-70°C), indicating a complex cationic composition possibly including Li+.

Overall, these data indicate that the early hydrothermal fluids at Rabenwald were extremely saline; later fluids evolved towards salinities below NaCl saturation. Deduced from isochores of the early fluids, the inclusions were trapped at minimum P/T conditions of 350°C and 3 kbars. MOINE et al. (1989) proposed talc formation at Rabenwald at 500–550°C and 8–9 kbars based on mineral equilibria and on fluid inclusion studies.

Here it is suggested, that these extremely high P/T conditions only occurred during an early evolution phase of the thrust plane containing the deposit, while actual talc formation took place later at lower P/T conditions somewhere above the minimum values derived from this study.

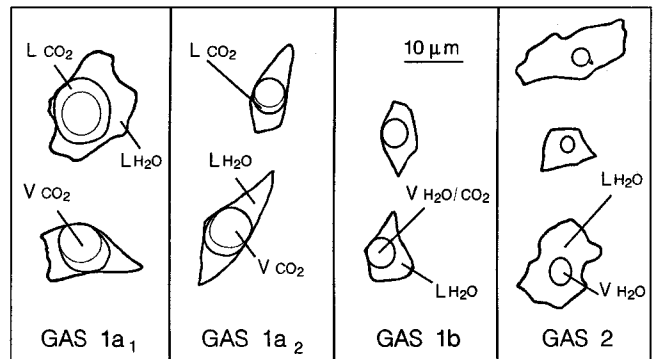
Samples from Hüttenberg included idiomorphic quartz crystals in siderite ore, and quartz from druses in the ore and from crosscutting veinlets. For comparison, quartz from hydrothermally altered pegmatite in the ore and from unmineralized, post-ore quartz veins was investigated. HÜ 1 fluids have been found in both the idiomorphic quartz crys-

Table 4.
Composition of evaporates of fluid inclusions in quartz from mineral deposits in the Eastern Alps, calculated to 100 wt % chloride. Analyses by REM/EDA.

Deposit	weight %				Others (traces)
	Na	Ca	K	Fe	
Mitterberg	35	2,7	traces	3	
Erzberg	23	12	5	3	(Al, Mn, Zn)
Schendleck	31	5	<1	2,1	(Mn, Al)
Kleinkogel	22	2,5	16	2,1	
Rabenwald	32	3,7	4,2	0,4	(Al, Mn, Ni, Cu)
Hüttenberg	23	5	2	3	
Waldenstein	31,6	4,7	2,4	0,6	
Gastein	29,6	-	4,2	-	

tals and in the pegmatite quartz. They are dominated by CH_4 and by CO_2 , with variable contents of an aqueous phase of low salinity (Table 3). HÜ 1a fluids homogenize into the liquid phase, while HÜ 1b inclusions show homogenization into a gas phase. This is considered to indicate unmixing of an originally homogeneous fluid. The purely aqueous HÜ 2 fluids characterize the idiomorphic quartz in siderite. Their salinity approaches the halite saturation. T_{FM} at -50°C and T_{M} hydrohalite at -28°C indicate a $\text{NaCl}/\text{CaCl}_2$ ratio of about 0,4. Upon heating, HÜ 2 inclusion homogenize into the liquid phase at $200\text{--}250^\circ\text{C}$. HÜ 3 inclusions were found in quartz sulfide veinlets cross-cutting the ore. They consist of an aqueous phase of moderate salinity, and of liquid and gaseous CO_2 . HÜ 3a inclusions are primary, while HÜ 3b occupy microfractures in the same samples. HÜ 4 and HÜ 5 inclusions are restricted to the late, unmineralized quartz veins. Both are primary inclusions and occur side by side. HÜ 4a inclusions are aqueous and saline with very little CO_2 , and contain several daughter minerals, including halite, calcite, tourmaline (?), and mirabilite (?). HÜ 4b inclusions are similar but without daughter crystals. HÜ 5 inclusions contain mainly liquid CO_2 and CH_4 , with very little water and, rarely, accidentally trapped halite crystals. HÜ 4 and 5 inclusions are probably products of unmixing of a common parent fluid. Estimates of the P/T conditions during the formation of the Hüttenberg deposit can be derived from HÜ 1, HÜ 2, and from HÜ 3 inclusions. Although pressure conditions must have been fluctuating widely by interference of tectonic activity along the fault zone with the hydrothermal system, the main phase of mineralization is reasonably constrained at about 2 kbars and at 350°C . Throughout the active time of the system recorded by the fluid inclusions, waters of widely varying salinity, liquid $\text{CO}_2\text{--CH}_4$, and less frequently gaseous $\text{CO}_2\text{--CH}_4$ were trapped. The main phase mineralization formed from moderately saline purely aqueous fluids. Early inclusions record high temperatures of about 480°C , while the latest inclusions may have been trapped at about 300°C .

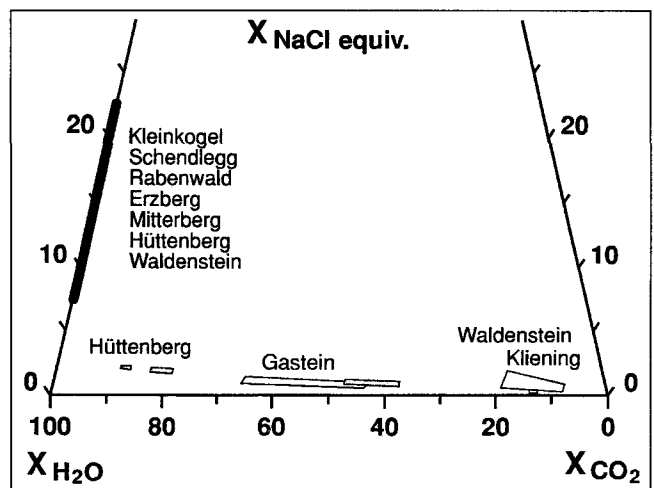
At Waldenstein, samples included quartz crystals from hematite-calcite-quartz druses in the ore, calcite from veinlets crosscutting the ore and from coarsely recrystallized country rock marble, and quartz from hydrothermally altered pegmatite. In all samples aqueous, primary, and high saline inclusions occur (WAL 1: Table 3). Two subgroups could be recognized. Most frequent are inclusions of the type WAL 1a with about 24 wt. % NaCl equivalent and homogenization into liquid phase at $135\text{--}260^\circ\text{C}$, while type WAL 1b with halite and calcite daughter minerals is rare. The latter reach salinities of 34 wt. % NaCl equivalent and homogenize at $130\text{--}200^\circ\text{C}$ into liquid phase. T_{FM} at -50°C and T_{M} hydrohalite at -28 to -36°C indicate an important content of CaCl_2 in addition to NaCl. Only microfractures in quartz of the druses appear to contain WAL 2 inclusions. These consist of liquid and gaseous CO_2 , and of water of variable salinity. Upon heating they homogenize into the gas phase. Clearly, the hydrothermal system was more water dominated than the one at Hüttenberg, although in both cases the main mineralization is associated with aqueous fluids. P/T conditions of ore formation can be constrained by isochores of WAL 1 fluids (BELOCKY, 1992) and by oxygen isotopic compositions of hematite-quartz pairs (PROCHASKA et al., in print) to about 300°C and 1,6 kbars, although pressure was probably fluctuating by interference with active faulting. It is tempting to attribute both the elevated salinity of the fluids and the oxydic nature of the mineralization to boiling. This remains equivocal, however, as inclusions of the appropriate low density have not been found.



Text-Fig. 3.
Fluid inclusion types in quartz of the gold-bearing shear zones at Gastein, as an example for CO_2 -rich fluids of the post-orogenic central Alpine fluid province.

At the former gold mine of Klüening quartz associated with sulfides was sampled for fluid investigations. Most inclusions found were moderately saline and aqueous, homogenizing into 1 liquid phase at $140\text{--}220^\circ\text{C}$ (type KLI 1: Table 3). T_{FM} down to -55°C and T_{M} hydrohalite at -22°C indicate a small content of CaCl_2 besides NaCl. Extremely rare are inclusions of type KLI 2 with liquid and gaseous CO_2 , and with water. Based on the isochores of KLI 1 (BELOCKY, 1992) and on the presence of cubanite with a minimum formation temperature of 250°C , the deposit was formed at 1 kbar or at higher pressures.

In the former gold mining district near Gastein quartz from the auriferous shear zones in Variscan granite gneiss was collected in the Imhof mine. Two fluid types can be differentiated (Text-Fig. 3. Table 3). GAS 1 inclusions contain both moderately saline water and CO_2 , while GAS 2 inclusions are purely aqueous with low salinities. The first forms both primary dispersed swarms and pseudo-secondary planes in quartz. It comprises a spectrum from CO_2 dominated fluids homogenizing into gaseous phase (GAS 1a1) to H_2O dominated inclusions where CO_2 can only be determined by clathrate formation, and which homogenize into liquid phase (GAS 1b). Type GAS 1a2 is intermediate in composition, it homogenizes into liquid phase. GAS 1 fluids are best understood as products of unmixing of a $\text{H}_2\text{O--CO}_2$ fluid which existed at about 420°C and 1 kbar when pressures were lowered by shearing to about 0,7 kbar. GAS 2 fluids occur in secondary planes only and are younger than the main phase of mineralization.



Text-Fig. 4.
Chemical variability of fluid inclusions in Alpidic mineral deposits in a ternary plot NaCl - H_2O - CO_2 .

4.2. Fluid Provinces

In spite of the wide variability of fluid inclusions in East Alpine mineral deposits described above it is possible to differentiate two different fluid families and, considering the tectonic and temporal setting, two fluid provinces:

- The fluids of the first are essentially aqueous brines, and they never contain CO₂ as a separate phase at room temperature (Text-Fig. 4). They have a high density, high filling rates, and most inclusion types contain halite daughter crystals. These fluids were found in the deposits at Mitterberg, Erzberg, Schendleck, Kleinkogel and Rabenwald. This group of deposits was traditionally thought to have formed in the Cretaceous, and stressing its structural setting they may be summarized as products of a "syn-orogenic Austroalpine fluid province".
- The second is characterized by the conspicuous presence of CO₂ (+CH₄) and by low to moderate salinities. Typically, these fluids often reflect unmixing of an originally homogeneous phase. These deposits (Hüttenberg, Waldenstein, Kliening, Gastein – see Text-Fig. 4) are of Tertiary age, they occur in both the Penninic and the Austroalpine domain, and because of this they are here proposed to have formed from a "post-orogenic central Alpine fluid province".

Evaporates of fluid inclusions were analysed by SEM/energy-dispersive X-ray fluorescence following the method described by HAYNES et al. (1988) in order to enlarge the data base on the chemical composition of the fluids. Measured percentages of cations contributing to salinity in fluid inclusions (Table 4) reflect primarily the local geological setting of individual deposits. Those in predominantly gneissic terrain have elevated K-contents. This is especially obvious for Kleinkogel, where chloritization and albitization of Variscan granites during Alpidic metamorphism evidently released K and Ba from K-feldspars and from biotites. In contrast to these chemical characteristics of the fluids acquired along their flow paths, in situ processes (the metasomatic ex-

change of Ca by Fe in the solid phase) are responsible for the elevated Ca-contents of fluids in metasomatic iron ore deposits like Erzberg.

Estimates of the most probable P/T-conditions of formation of the individual deposits (Table 5) are based on isochores of fluid inclusions calculated according to BOWERS & HELGESON (1983), NICHOLLS & CAWFORD (1985) and BROWN & LAMB (1989), combined with geological constraints. From these data, a general trend emerges: one group of deposits formed at higher pressures, which is identical with the first described above, and a second group formed at lower pressures, comprising the central alpine deposits.

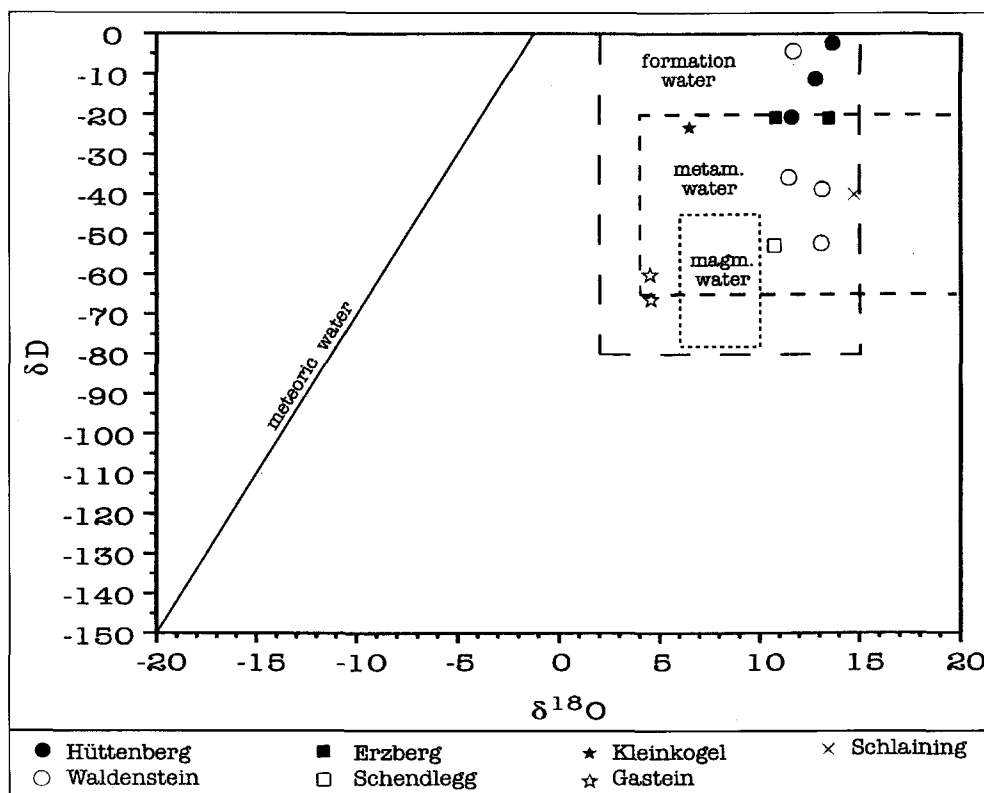
5. Isotopic Data

The derivation of fluids moving in the crust, their interactions with rocks along flowpaths, and conditions of mineral precipitation can often be traced using appropriate isotope systems. For this study, a limited number of hydrogen, oxygen and carbon isotopic compositions of fluids responsible for the formation of East Alpine mineral deposits were determined.

Hydrogen was extracted from fluid inclusions by thermal decrepitation of quartz samples followed by reduction with Zn (COLEMAN et al., 1982). The isotopic ratio D/H of the hydrogen gas produced was measured on a Finnigan MAT 251 mass spectrometer. Oxygen was extracted from hydrothermal quartz and carbonates following the methods of BOTHWICK & HARMON (1982) and McCREA 1950). The ¹⁸O/¹⁶O ratios of aqueous fluids in equilibrium with these minerals were then calculated for estimated formation temperatures of the individual deposits (or minerals) using currently accepted fractionation factors.

Carbon isotopes (¹³C/¹²C) were either determined by thermal decrepitation of CO₂-rich inclusions similar to hydrogen, or concurrently with the determination of oxygen isotopes of carbonates.

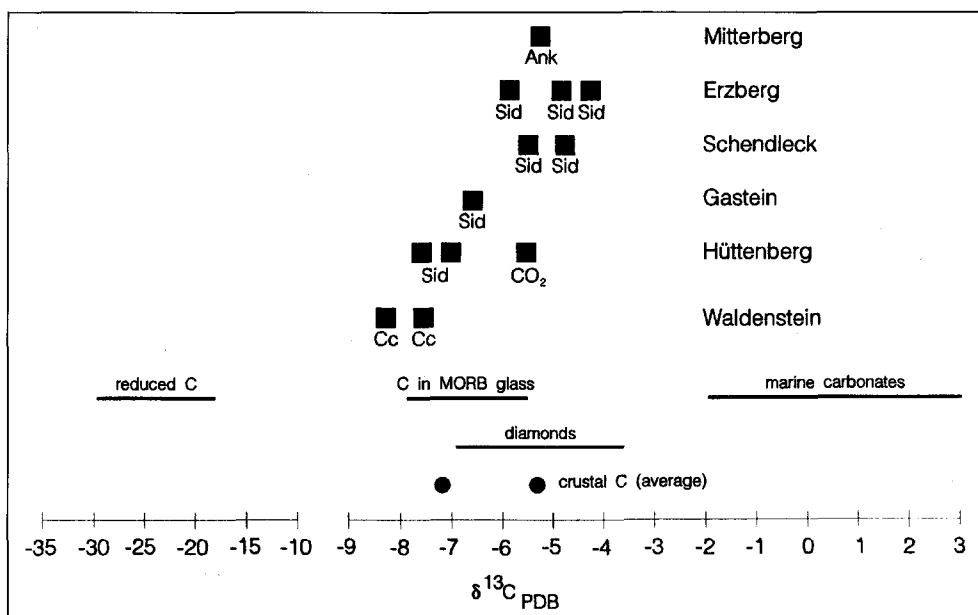
Comparison of the isotopic composition of water in hydrothermal fluids having formed mineral deposits in the Eastern Alps with typical fields of crustal water (Text-Fig. 5) allows the general conclusion, that equilibration of different waters with large amounts of crustal rocks was a dominant process. Neither "primitive", little evolved waters of oceanic or meteoric origin were involved, nor unequivocal magmatic waters. The data of the fluids of the syn-orogenic Austroalpine pro-



Text-Fig. 5. Isotopic composition of water in fluids having formed Alpidic mineral deposits in the Eastern Alps. Delimitation of typical water fields according to HOEFS (1987).

Text-Fig. 6.

Isotopic composition of carbonates and CO₂ from mineral deposits of the Eastern Alps. Ank = ankerite, Sid = siderite, Cc = calcite. Comparative data are from KERRICH & FENG (1992).



vince (Erzberg, Kleinkogel, Schendleck) clearly plot into the metamorphic field, while those of the post-orogenic central province (Gastein, Hüttenberg, Waldenstein) spread over the fields of metamorphic and of formation waters. This is due to a wide variance of δD in these fluids, which may be explained by non-homogeneous sources of the water (meteoric or sea water, possibly mixing with metamorphogenic water from depth). Distinctly lower $\delta^{18}O$ of the fluids at Kleinkogel and at Gastein can be shown to result from equilibration of the fluids with (meta-) granites, which surround or underlie these deposits (BELLICKY, 1992).

Carbon isotopic compositions of CO₂ or of carbonates (Text-Fig. 6) fall into two groups again. Siderites from the deposits at Erzberg, Schendleck and Mitterberg have $\delta^{13}C$ of -4 to -6, while values from -6 to -8 characterize CO₂ and carbonates from Gastein, Hüttenberg, and Waldenstein. These data are compatible with the variation fields given by SCHROLL (1990) and by SPINDLER (1992). Although local influences from carbonatic country rocks at individual deposits will not have been without influence, these preliminary data indicate quite homogeneous carbon systems for both groups of deposits. Generally, the clustering of the data about average values for crustal carbon point to a carbon source involving homogenization of carbon derived from large volumes of crustal rocks. The slightly lighter carbon of the central province might also be derived from mantle sources.

6. Discussion and Conclusions

Mainly because of geological observations, major orogenic and metamorphic phases in the Eastern Alps were considered earlier to have caused epigenetic hydrothermal mineralization. The present investigation of fluid inclusions and stable isotope systems of typical examples of deposits attributed to this group reveals two distinct fluid families. As each of these fluid families is restricted to a specific setting in time and in space related to the evolution of the Eastern Alps, they are here considered to represent two different fluid pulses as well as two provinces:

The first occurs mainly along the northern margin of the Austroalpine nappe pile, affecting all of its three major tectonic units, but not the underlying Penninic. These fluids are highly saline and of elevated density. The CO₂ content is very low. Their water is most probably of metamorphic origin. Carbon isotopes of vein carbonates indicate a carbon source characterized by homogenization over large vol-

umes of sedimentary rocks. Estimated pressures at the sites of mineralization are in the order of 2–4 kbars, at predominantly lithostatic conditions. Deposits formed by these fluids include Erzberg, Mitterberg, Schendleck, Kleinkogel, and Rabenwald. Constraints on the time of this fluid pulse are

- 1 the age determination on uraninite from Mitterberg (90 Ma), and
- 2 cross-cutting relations of mineralization with early Cretaceous schistosity (Erzberg, Schendleck, Mitterberg).

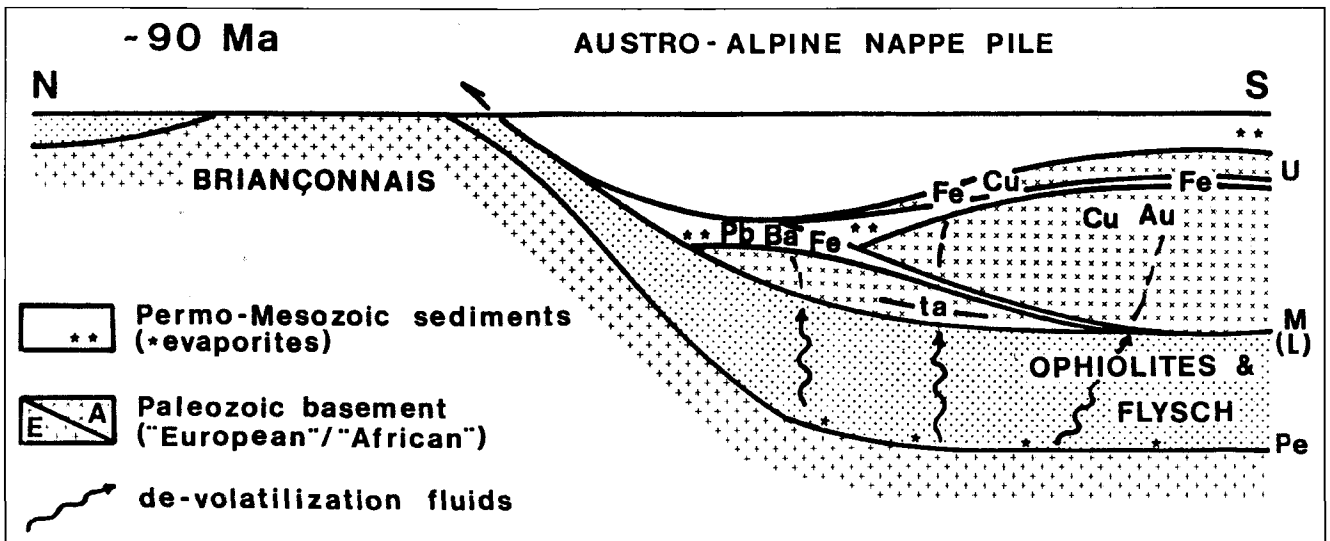
The tectonic control is ductile deformation in the Lower Austroalpine (Rabenwald), but brittle at tectonically higher levels (Mitterberg, Schendleck, Kleinkogel). Because of the restriction of deposits formed from these fluids to the Austroalpine tectonic units, and in view of the coincidence of this fluid pulse with the first, Upper Cretaceous orogenic climax of the Eastern Alps it is here termed the “syn-orogenic Austroalpine fluid province”.

Table 5. Estimates of P/T conditions for the formation of investigated deposits.

Deposit	Pressure (kbar)	Temperature (°C)	Notes
Mitterberg	≥ 2	≥ 240	from dissolution of halite
Erzberg	c. 2-2,5	c. 250	not well constrained
Schendleck	≤ 3.5	≤ 250	not well constrained
Kleinkogel	> 1.5	> 150-200	halite dissolution
Rabenwald	≥ 3	≥ 350	halite dissolution
Hüttenberg	c. 2	c. 350	relatively well constrained
Waldenstein	1,6	300	oxygen isotopes *)
Klienig	c. 1-1,9	c. 250-300	
Gastein	≤ 1-0,7	420-200 **)	unmixing by seismic pumping

*) Based on oxygen isotope equilibration temperatures (PROCHASKA et al., in print).

**) For a detailed discussion of mineralization temperatures see CRAW et al. (1993).

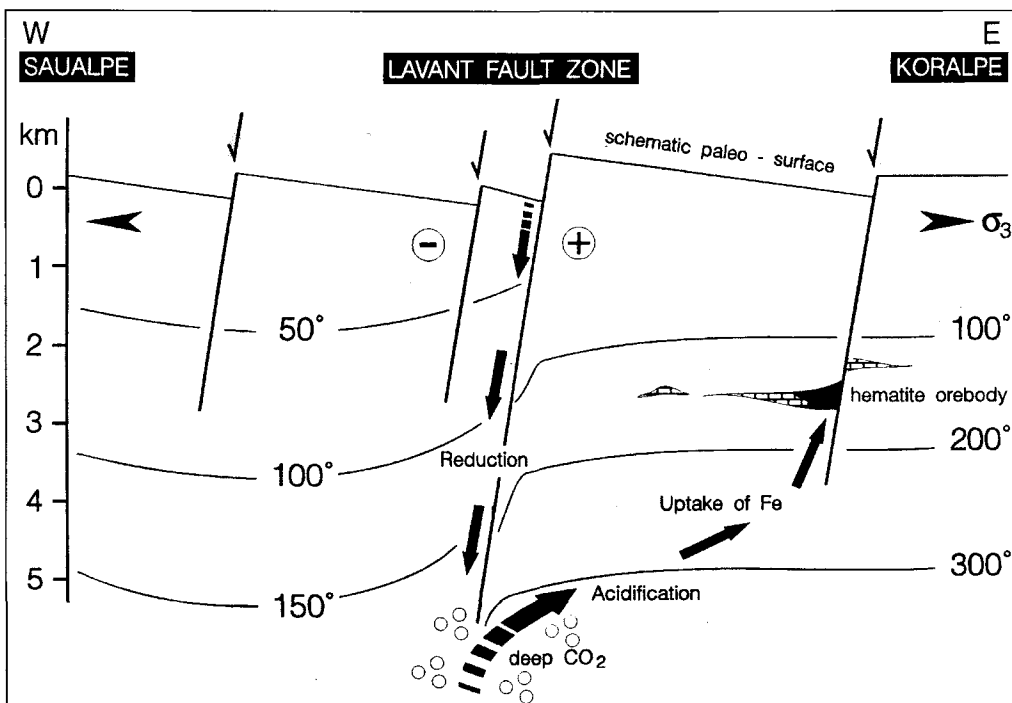


Text-Fig. 7. Model of Upper Cretaceous (ca. 90 Ma) collision in the Eastern Alps and mineralizations of the syn-orogenic Austroalpine province induced by prograde devolatilization fluids. ta = talc at Rabenwald. Pe = Penninic. L, M, U = Lower, Middle, Upper Austroalpine tectonic unit.

The second fluid province appears in the central parts of the Eastern Alps only, affecting both the Penninic as well as the overlying Austroalpine units. Deposits representing this fluid province are Gastein, Hüttenberg, Waldenstein, and Klüning. The fluids always contain CO₂ (plus CH₄ at Hüttenberg), and frequently show signs of unmixing. Salinities vary from low to moderate. Typically, gold depositing fluids have low salinity (Gastein, Klüning), while those with elevated salt contents occur in the iron ore deposits (Hüttenberg, Waldenstein). The solutes were probably derived from interaction of hydrothermal fluids with country rocks along the flow paths, thus causing retrograde metamorphism. With widely varying δD, their water may involve various components, including meteoric, marine, and metamorphic sources. The isotopic composition of carbon is lighter here than in the synorogenic province, and is very close to the crustal or mantle average. Both reservoirs are a possible

carbon source for these fluids. Ambient pressures during mineralization (< 2 kbar) are generally lower for this group than for the first. By interaction with faulting, the pressures may have varied between near lithostatic to near hydrostatic. The exact age of these mineralizations is not well constrained. Their tectonic control by brittle deformation following nealpine orogeny and metamorphism, however, as most clearly seen at Gastein, indicates an age of < 30 Ma. Based on the occurrence of deposits formed from comparable fluids throughout the central Eastern Alps and on their formation after the second, Eocene orogenic climax, it is proposed to summarize these mineralizations as having been formed from a "postorogenic central Alpine fluid province".

Combining geological background information with our new data on the synorogenic Austroalpine fluid province the following genetic model is proposed (Text-Fig. 7): During the Late Cretaceous (probably Turonian: c. 90 Ma), subduction had consumed the South Penninic ocean and the Austroalpine nappe pile collided with the Middle Penninic Briançonnais. During subduction some South Penninic rocks but also parts of



Text-Fig. 8. Genetic model of the Waldenstein hematite deposit as an example for the post-orogenic central alpine province showing relations between Tertiary trans-tensional structures, fluid convection cells, and retrograde metamorphism. Black arrows indicate fluid movement.

the Austroalpine unit suffered high pressure metamorphism (eclogites, blueschists). Most of the Flysch sediments deposited concurrently, as well as the sedimentary platform cover of the Briançonnais, were metamorphosed and devolatilized shortly before and during the collision for the first time. Within the South Penninic zone (and through large areas of the Austroalpine domain), Permo-Mesozoic evaporitic sediments are ubiquitous, representing a probable source for the high NaCl-contents of the fluids, which is unusual for prograde metamorphic fluids. The fluids were possibly ponded until a relaxation phase immediately following collision allowed their escape. The migration paths may have included thrust zones as at Rabenwald. Generally, the fluids flowed rapidly into higher parts of the nappe pile, where discrete brittle structures (Mitterberg, Schendeleck, Kieinogel), or impermeable caprocks on domal structures (Erzberg) provided physical and chemical conditions for mineralization.

A conceptual model of the environment in which the hematite deposit Waldenstein was formed shall serve as an example for the more variable settings of individual deposits of the postorogenic central Alpine fluid province (Text-Fig. 8). In the Waldenstein-Hüttenberg district, transtensional faulting and tilting of blocks along the Lavant and Görtsschitz fault zones produced thermal anomalies as well as pathways for surface-fed fluid convection cells and for fluids ($\text{CO}_2 \pm \text{CH}_4 \text{ H}_2\text{O}$) rising from deeper crustal and possibly even mantle levels. Parts of the deep fluids may have been ponded metamorphic fluids produced within the Penninic rocks underlying the Austroalpine unit during the Eocene orogeny. Considering the predominance of Fe (second to NaCl, of course) as a solute in these fluids, they must have been reducing and acid when leaching Fe from rocks at depth. Retrograde formation of hydrous minerals in the pervaded amphibolite facies suite would have led to the observed salinities (BENNET & HARKER, 1992) which range from moderate to elevated. Fluids of high salinity at Waldenstein as well as the oxydic nature of the mineralization, which is rare in the mainly sideritic iron ore province of Hüttenberg-Waldenstein, could best be explained by boiling. However, evidence for such a process is missing, and the difference between the strongly reduced fluids at Hüttenberg (with CH_4) and the oxydized fluids Waldenstein (CO_2) must be sought in the evolution of the fluids below the level of mineralization. Possibly the hydrothermal system at Waldenstein has drawn in waters from different levels, including more oxygenated surface waters with a short flow distance in the sub-surface.

Overall it may be concluded, that both earlier tentative interpretations as well as our data support a genetic connection between major periods of Alpidic metamorphism and mineralization in the Eastern Alps. Deposits related to the Cretaceous orogeny conform to the model of hydrothermal fluids derived from metamorphic devolatilization, while those related to the Tertiary orogenic phase can be interpreted as products of retrograde metamorphic leaching (POHL, 1992a).

Acknowledgements

The project was financially supported by the German Research Fund (DFG). We are grateful to W. PAPESCH and D. RANK for access to the mass spectrometer laboratory of the Geotechnical Institute Arsenal, Vienna, Austria. J. HOEFS, Göttingen, provided oxygen isotope analyses on quartz samples. W. FRISCH, Tübingen, G. FRIEDRICH, Aachen, and W. PROCHASKA, Leoben, kindly read and improved the paper.

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Manuscript received: 21. 09. 1992 ●

Revised version received: 02. 06. 1993 ●

Manuscript accepted: 28. 06. 1993 ●

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Zeitschrift/Journal: [Austrian Journal of Earth Sciences](#)

Jahr/Year: 1993

Band/Volume: [86](#)

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Artikel/Article: [Alpidic Metamorphic Fluids and Metallogensis in the Eastern Alps. 141-152](#)