

The fluorite vein mineralization of the southern Alps: combined application of fluid inclusions and rare earth element (REE) distribution

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Abstract

The fluorite vein deposits of the Southern Alps (Northern Italy) exhibit similar geotectonic, paragenetic, and textural characteristics permitting useful comparison between their fluid inclusions and REE systematics. Due to differing post-crystallization deformation, primary fluid inclusions can only be observed in the northernmost deposit (Rabenstein/Corvara). Here, fluorite precipitated from highly saline $H_2O-NaCl-CaCl_2$ solutions containing appreciable H_2S . During vein formation the fluids changed from low salinity (≈ 7 wt. % NaCl equiv.) and medium temperature ($T_h \approx 230^\circ C$), corresponding to the precipitation of early quartz, towards high salinity (≈ 20 wt. % NaCl equiv.) and lower temperatures ($T_h \approx 170^\circ C$) during the deposition of late-stage fluorite. This was accompanied by an increase in Ca in solution.

REE distribution patterns for the northern deposits are very uniform suggesting a similar source, a large-scale homogeneous fluid system, and fluorite precipitation under reducing conditions. By comparison the southern deposits exhibit contrasting patterns documenting a more complex history, probably due to their remobilization from an earlier mineralization. None of the fluorites shows a 'primary' magmatic REE distribution pattern, thereby favouring a genetic model for fluorite mineralization involving the leaching of suitable rock units by formation waters.

KEYWORDS: fluorite, vein mineralization, fluid inclusions, Alps, rare earth elements.

Introduction

THE FLUORITE vein deposits of the Southern Alps (Northern Italy) have contributed considerably to Italy's past fluorite production, and a few of them are still being mined. The mineralizations exhibit a number of comparative characteristics:

- i. Most of the veins are spatially connected (Fig. 1) with either Late Variscan granitoids of the pre-Permian basement and/or acid Permian volcanics (Omenetto and Brigo, 1981).

- ii. The multi-stage veins display a simple and uniform paragenesis. Massive fluorite is by far the predominant mineral making up to 90% of the

veins. Quartz is commonly a precursor to the mineralization and occurs in different 'generations', often replacing earlier fluorite. Calcite and rare dolomite occur locally and siderite is particularly noticeable in the Val Trompia region. Baryte is rare and usually late in the paragenesis. Generally, the sulphide content is a little higher in the basement-hosted veins (Omenetto and Brigo, 1981).

- iii. Primary textures as cockades, rhythmic banding, crystal zoning, and syngenetic brecciation are common and point to periodic and rapid changes of the physico-chemical conditions during mineral precipitation. Postcrystalline deformation of varying intensity can be observed in all deposits. Mild deformation is documented by undulatory extinction of quartz crystals, weak anisotropy of

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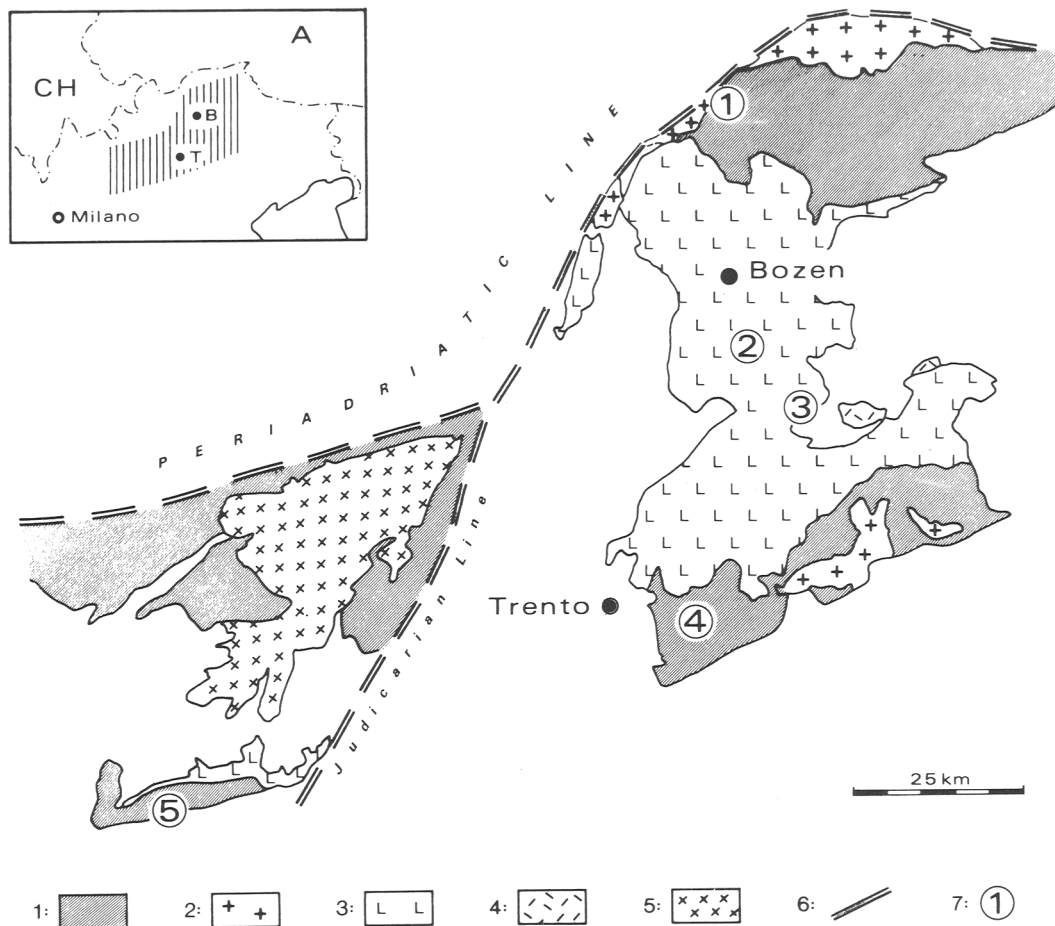


FIG. 1. Distribution of magmatic rock south of the Periadriatic Line (Southern Alps, Northern Italy) and location of the major fluorite vein deposits in the Bozen-Trento region and the Val Trompia respectively. Legend; 1, South Alpine pre-Permian metamorphic basement; 2, Late Variscan granitoids; 3, Permian volcanites ('Bozen quartz porphyries'); 4, Triassic intrusives of the Dolomites (Predazzo-Monzoni); 5, Alpidic granodiorite (Adamello); 6, Major faults; 7, Fluorite deposits, (1) Rabenstein/Corvara, (2) Brantental/Vallarsa, (3) Prestavel, (4) Vignola, (5) Torgola.

the sulphides, or fluorite twinning lamellae parallel to (100). With increasing intensity the veins are internally fractured. In the Bozen-Trento area primary textures are best preserved at Rabenstein/Corvara, and vein deformation seems to increase southwards. The Torgola veins exhibit the highest degree of deformation; primary textures are almost completely obliterated, and fluorite is recrystallized to transparent layers which are free of primary fluid inclusions.

Of the numerous occurrences, the deposits of Rabenstein/Corvara, Brantental/Vallarsa, and

Prestavel in the Bozen area, Vignola near Trento, and Torgola in the Upper Val Trompia north of Brescia were chosen for this study.

Regional geological framework

The mineralization of Rabenstein/Corvara is hosted by mica-shales and phyllites of the Southern Alps metamorphic basement (Krahmann, 1906) in the immediate vicinity of the Iffinger granodiorite (301–230 Ma; Sassi *et al.*, 1985). The fluorite veins follow a system of faults which run almost parallel to the nearby Periadriatic line,

being additionally traced by acid to basic dykes in the aureole of the Iffinger intrusion. Kersantitic lamprophyres of unknown age cut the mineralization. Massive fluorite from Rabenstein/Corvara is commonly of grey to slightly greenish and occasionally of pinkish grey colour. Late fluorite is grey to white and occurs locally as open space fillings or as free grown crystals with remarkably faceted habits in vugs.

At *Brantental/Vallarsa* a subvertical vein cuts rhyolitic ignimbrites of the 'Bozen quartz porphyries' which is the highest volcanic unit in the sequence and extends into the overlying Upper Permian 'Gröden sandstone' (Perna, 1964). Massive fluorite is commonly of grey colour. Partial rhythmic growth banding can be observed.

The *Prestavel mine* worked two fluorite bodies hosted by rhyolitic ignimbrites of the upper sequence of the 'Bozen quartz porphyries'. The mineralization cuts intercalated alkaline-porphyrific dykes of Ladinian age (Perna, 1971) and consists mostly of massive fluorite and quartz.

At *Vignola* four veins occur along the northern flank of the Cima d'Asta anticline (285–268 Ma; Sassi *et al.*, 1985), hosted by intensively albitized paragneisses and quartz-phyllites of the metamorphic basement. The major vein is affected by strong deformation and is cut by a younger baryte vein. Fluorite is commonly of greyish-white colour and massive, although vugs with pinkish crystals up to 10 cm in size have been reported (Perna, 1964).

The *Torgola vein deposit* is located in the Upper Val Trompia, 40 km north of Brescia. Here, a granodiorite (222 Ma; Sassi *et al.*, 1985) is intruded into phyllites and gneisses of the metamorphic basement. The mineralization cuts the phyllites and the roof of the Val Trompia granodiorite cupola as well as the overlying Upper Permian 'Verrucano Lombardo'. The nearby fluorite vein of *Pezzaze* even extends into marls of the Lower Triassic Collio formation. Locally, the veins attained a remarkable thickness of up to 18 m (Bianchi *et al.*, 1971).

Sampling and analytical procedure

In situ fluorite samples were collected from the active mines of Rabenstein/Corvara and Brantental/Vallarsa. At the Torgola mine two profiles crossed the 'Torgolino 2' fluorite body at a vertical distance of 26 m. Microthermometric measurements were made using modified versions of commercial CHAIX-MECA (Institute of Applied Geology, Free University, Berlin) and LINK-HAM TH 600 (Department of Petrology, Technical University) equipment. Instrumental neutron

activation analysis was carried out at the Hahn-Meitner-Institute, Berlin.

Fluid inclusion petrology

Due to post-crystalline deformation of varying intensity, primary fluid inclusions are rare in the fluorites and can usually be observed as relics only.

At *Rabenstein/Corvara* no unequivocally primary inclusions suitable for microthermometry were detected in the massive fluorite despite favourable conditions afforded by epitactic overgrowths of sphalerite on fluorite cube-faces or occasional relics of growth zoning. However, late fluorite crystals exhibit excellent primary inclusions which can be subdivided into 'early' and 'late' due to their position in the fluorite cubes.

Early primary inclusions are rare and usually isolated. Only 4 measurements were obtained. Usually the inclusions are 10–40 μm long, but may reach 120 μm in size. Their shape is simple, often elongated, and characterized by cube faces which are sometimes rounded (Fig 2a). At room temperature they contain an aqueous solution and a vapour bubble which is surrounded by a thin rim of a second immiscible liquid. In a few cases only, tiny birefringent daughter crystals were observed, which are situated either in the immiscible-liquid film or at the inclusion walls.

Late primary inclusions commonly decorate growth zones parallel to (100) and/or syngenetic cracks. Compared to the early primaries, their shapes are more irregular (Fig. 2b,c). Often tiny, narrow channels connect 'isolated' larger inclusions, indicating periods of irregular, rapid growth during the latest stage of mineralization, probably caused by pulsatory changes in the dynamics of the fluid system. In a few cases 'necking' resulted in inclusions with variable phase ratios. The latter were disregarded for microthermometric measurements. In size, the late primaries range from a few μm up to 120 μm . At room temperature they contain the same phases as the early primaries, except that the immiscible liquid occupies a smaller volume, often being just visible, and tiny, elongated, birefringent crystals are more common in the fluid inclusions and as occasional solid inclusions in the same or neighbouring growth zones. No discernible volume changes of these crystals occurred in the inclusions during the heating and freezing runs, which suggests that they are trapped solids rather than true daughter minerals. These crystals were subsequently identified as baryte by SEM-EDS techniques.

No primary inclusions of suitable quality for thermometric analysis were found in samples from *Brantental/Vallarsa*, *Prestavel*, and *Vignola*

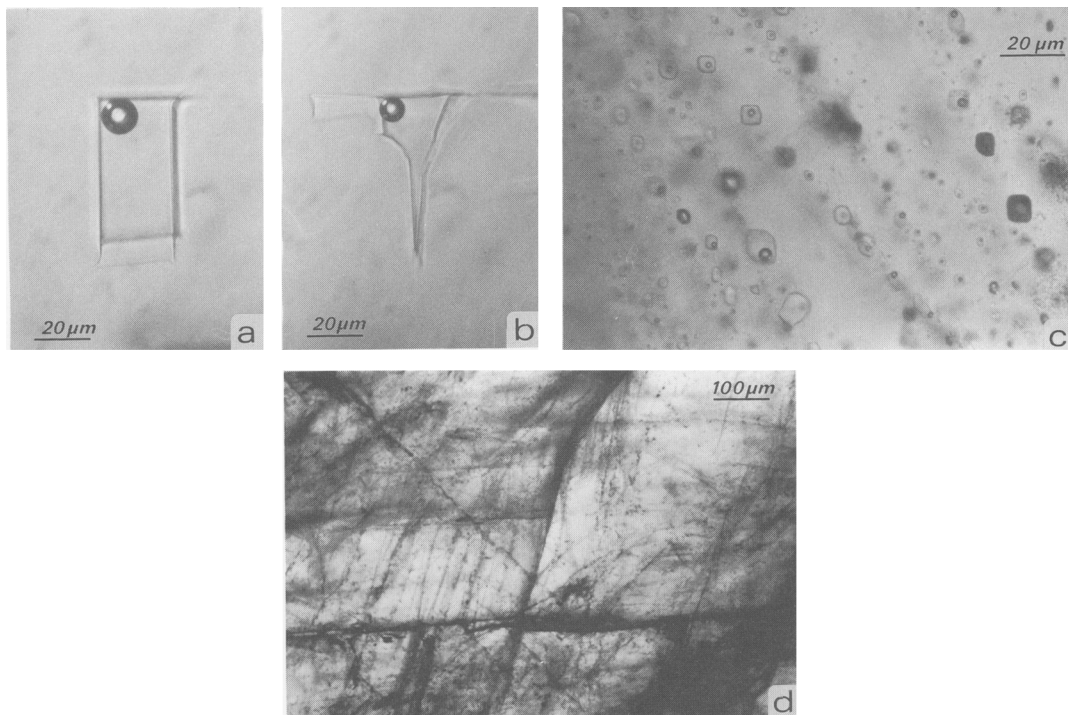


Fig. 2. (a) Cube-faced early primary fluid inclusion in fluorite (for details see text). Rabenstein/Corvara, doubly polished thick section (DPTS), polarizers parallel (PLP). (b) Late primary fluid inclusion in fluorite (for details see text). Rabenstein/Corvara, DPTS, PLP. (c) Trails of pseudosecondary to secondary fluid inclusions (negative crystal shape) parallel to (111) in late-stage fluorite. Dark inclusions close to the surface underwent secondary leakage. Rabenstein/Corvara, DPTS, PLP. (d) Trails of secondary fluid inclusions parallel to the cleavage of fluorite. Rabenstein/Corvara, DPTS, PLP.

even in fluorite cubes with growth zoning developed on (100) and (111). A weak deformation is shown by epigenetic opening and refilling along channels which are still open or only weakly recrystallized.

Primary inclusions along quartz crystal growth zones were observed in only one specimen of early quartz from Rabenstein/Corvara. In all other deposits inclusions in quartz were too small ($<5\ \mu\text{m}$) to be used for microthermometry.

Microthermometry

The immiscible liquid. During rapid cooling, 'double freezing' was observed in inclusions containing an immiscible liquid visible at room temperature. As fetid odours escaped during preparation of the samples, the composition of this liquid was suspected to contain H_2S . On warming, unequivocal triple melting was observed in a few, early primary inclusions between -82.2 and -81.2°C . This is close to the

triple point (-83.6°C) of pure H_2S (Bierlein and Kay, 1953). Single values for late primary inclusions range from -78.8 to -72.8°C , indicating a change in the immiscible liquid composition. However, due to poor optical definition, these few values represent exceptions and should not be overemphasized, as the first appearance of the immiscible liquid was frequently accompanied by immediate clathration (cf. Touray and Guilhaumou, 1984). During preliminary tests by Raman spectroscopy, the immiscible liquid was qualitatively verified to contain predominately H_2S , which agrees well with the fetid odours noted during sample preparation. Possible additional components were below the detection limit.

The aqueous phase. Most of the eutectic temperatures (T_e) obtained extend down to -54°C , which is below the eutectic of the pure H_2O - NaCl system (Sourirajan and Kennedy, 1962) and requires the presence of additional cations besides sodium. A few T_e measurements were even lower (Fig. 4). As reported by Walther (1981), the first

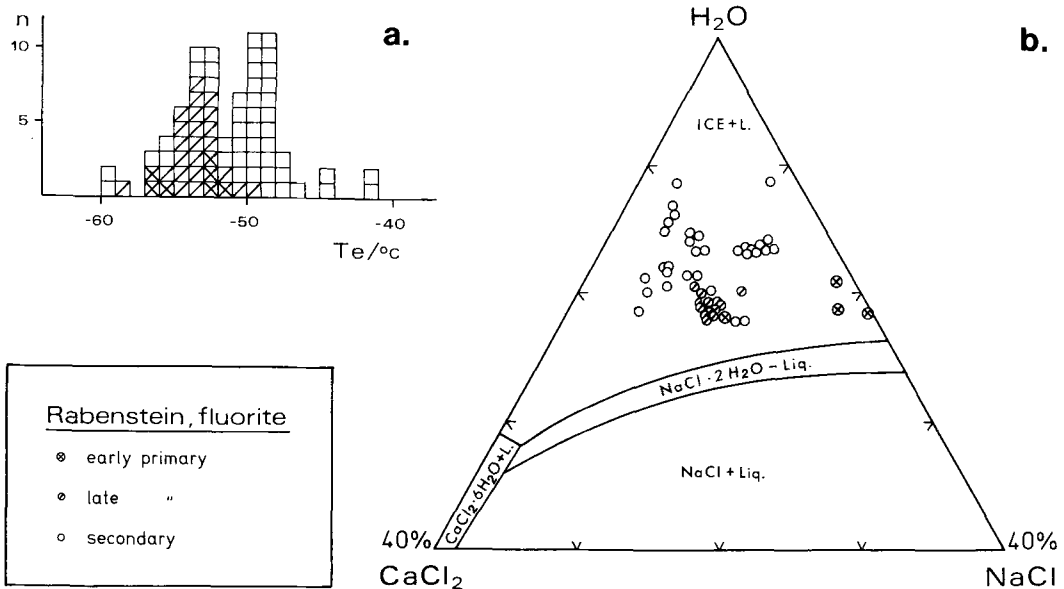


FIG. 3. Fluid compositions at Rabenstein/Corvara: (a) Histogram of eutectic temperatures (T_e); (b) Compositional development in the system H_2O - $NaCl$ - $CaCl_2$.

appearance of a liquid in a frozen inclusion of a given size is visible only if it occupies about 10 vol. % of the inclusion. Thus, the true eutectics may be lower than the T_e reported. If this is so, then the presence of additional ions, such as Li or Br (Borisenko 1978), is suggested. Upon warming, a hydrate phase, probably hydrohalite, melts incongruently to ice. Both eutectic temperatures and melting behaviour permit a first approximation of the fluid composition to the system H_2O - $NaCl$ - $CaCl_2$ / $MgCl_2$ (Yanatieva, 1946). A semi-quantitative analysis of the evaporate residues of selectively isolated and opened primary fluid inclusions by SEM-EDS confirmed the presence of Na, Ca,¹ and Cl as main constituents. No Mg was detected.

Coupled hydrohalite and ice melting temperatures (Crawford, 1981) document a compositional shift of the fluids in the system H_2O - $NaCl$ - $CaCl_2$ during mineralization at Rabenstein/Corvara (Fig. 3). While early quartz grew from low salinity (≈ 7 wt. %) H_2O - $NaCl$ fluids, massive fluorite precipitated from a highly saline H_2O - $NaCl$ ($\pm CaCl_2$) solution ($NaCl/CaCl_2$ wt. ratio >9). During the final mineralization stage (late primary

inclusions), the relative salinity (or chlorinity) remained constant (≈ 20 wt. % $NaCl$ equiv., corresponding to a chlorinity of 3.5 m $[Cl^-]$; Lüders, 1988), but the composition of the mineralizing fluid changed towards a higher $CaCl_2$ fraction ($NaCl/CaCl_2$ wt. ratio = 1). Secondary inclusions scatter over a wide compositional range suggesting dilution by less saline solutions during post-crystalline processes.

According to the presence of H_2S -clathrates, the absolute salinities inferred from the H_2O - $NaCl$ - $CaCl_2$ triangle are perhaps too high. Clathrate melting was observed in a few early and late primary inclusions only between -3.5 and $-1.3^\circ C$. As experimental data are lacking for the system H_2S - H_2O - $NaCl$ - $CaCl_2$, salinities were not corrected and only relative changes are taken into account. Because of its low volume proportion and corresponding optical limitations, neither homogenization behaviour nor partial homogenization of the immiscible H_2S phase could be recorded accurately. Thus, little information can be deduced regarding its influence on the total density of the mineralizing fluids.

All inclusions homogenize into liquid state, no 'boiling' was observed. This is consistent with the inferred depth of emplacement since a minimum overburden of approximately 150–200 m only (hydrostatic and/or lithostatic) would have been sufficient to prevent boiling during vein forma-

¹ By varying the focus and the acceleration voltage of the electron microbeam, it was possible to record the Ca of the evaporates only and not the background fluorite.

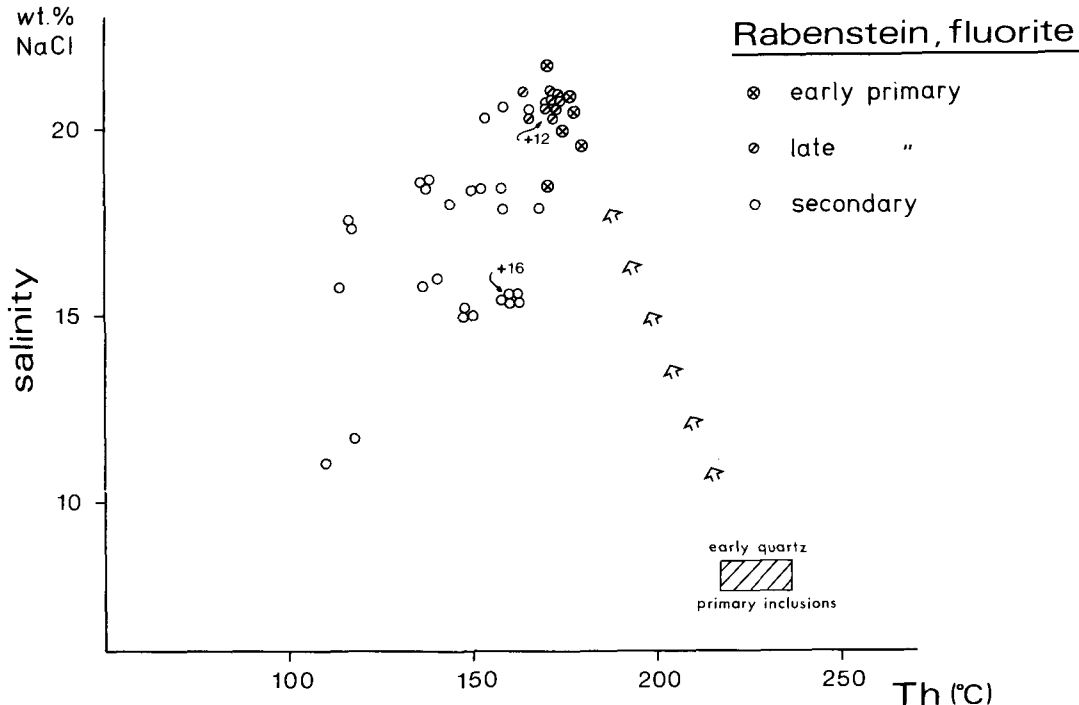


Fig. 4. Temperature of homogenization (Th) vs. salinity plot of different fluid inclusion generations from Rabenstein/Corvara.

tion. So, the homogenization temperatures are close to the trapping temperatures and need little or no correction. As shown in Fig. 4, the variation in temperature and salinity indicates evolution of the fluid system from relatively higher temperatures (early quartz, Th \approx 230°C) and low salinities towards lower temperatures (Th \approx 170°C) and maximum salinities around 20 wt.% NaCl equiv. (i.e. chlorinities of 3.5 m [Cl⁻]). Secondary inclusions again document dilution of the fluids and decreasing temperatures during epigenetic processes.

Rare earth element (REE) fractionation

By their ionic radii, trivalent REE are the principal trace elements in Ca-minerals. Because of their similar chemical behaviour, they are not separated from each other but only fractionated in hydrothermal systems. Details on the incorporation of REE into Ca-minerals during hydrothermal processes are given by Möller (1983).

By their REE distribution patterns two main groups of South Alpine hydrothermal vein fluorites are discernible. The patterns of early, massive fluorites from the northern deposits of Rabenstein/Corvara, Brantental/Vallarsa, and Prestavel

are more or less very similar (Fig. 5a), all exhibiting negative Eu anomalies. The only exception is one late-stage fluorite from Rabenstein/Corvara, the pattern of which runs almost parallel to those of the massive fluorites, but with no negative Eu anomaly. By comparison, the patterns of fluorites from the southern deposits, Vignola and Torgola, differ clearly (Fig. 5b) by showing an enrichment of the HREE and no negative Eu anomalies.

In addition, a number of host-rocks have also been analysed (Fig. 5c). The patterns of basement samples (Rabenstein/Corvara, Vignola) follow those of common metamorphic rocks. Those of the volcanics from both units of the 'Bozen quartz porphyry' and the Permian Val Trompia granodiorite are also similar. By their pronounced negative Eu anomaly, the highest degree of magmatic fractionation (Möller and Muecke, 1984) is indicated for rhyolitic ignimbrites of the upper volcanic unit.

Discussion

Previous discussions of the South Alpine fluorite veins implied a genetic relationship with the nearby granitic to granodioritic intrusions

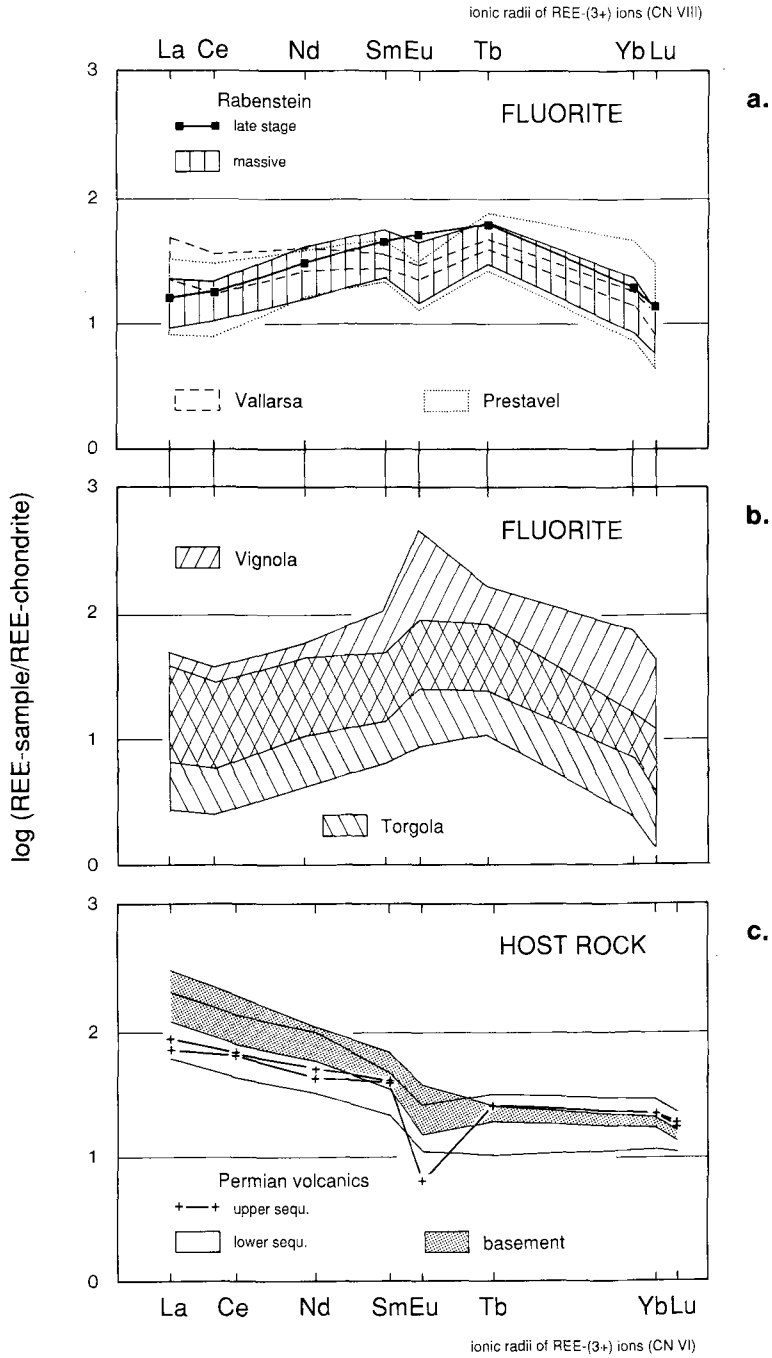


Fig. 5. REE distribution patterns of South Alpine vein fluorites (a northern deposits; b southern deposits) and corresponding host rocks (c).

(Fig. 1), which until the late 1960s were assumed to be Alpidic. However, radiometric dating of these plutons proved their Variscan (= pre-Alpidic) age (Sassi *et al.*, 1985). The following time markers must be taken into account:

- i. Earliest fluorite is reported as eroded fragments of quartz-fluorite veins in basal conglomerates of the Upper Permian 'Gröden sandstone' (Haditsch and Mostler, 1982).
- ii. Fluorite veins of the upper Val Trompia intersect strata of Lower Triassic age.
- iii. The Prestavel veins cut alkaline dykes which, by their composition, are believed to be Triassic (Perna, 1971).
- iv. The most intensive deformation phenomena can be observed at the southern deposits of Vignola, in the vicinity of the Val Sugana line, and especially at Torgola, along the Val Trompia line respectively. Both faults were active during Eoalpidic deformation (Doglioni and Bosellini, 1987).

Thus it follows that fluorite formation succeeded a long lasting thermal event, which started with Permian volcanism and possibly continued until the Mid-Triassic (second thermal maximum with magmatism and wide spread volcanism) and even longer (Ferrara and Innocenti, 1974; Sassi *et al.*, 1985). Upper Triassic, carbonate-hosted, Pb-Zn mineralizations bear fluorite as a minor to major constituent throughout the Southern and the Eastern Alps respectively (Omenetto and Brigo, 1981; Hein, 1986, 1989).

On the basis of the present study, none of the *REE* patterns in fluorite can be interpreted in terms of typical 'primary', magmatic precipitates because of their relatively low *LREE* contents. Consequently, a genetic relationship between fluorite mineralization and either Permian calc-alkaline volcanism or Triassic alkaline magmatism/volcanism (Bakos *et al.*, 1972) can be ruled out, even if the latter seems to be indicated with respect to F and *REE* (Gallitelli and Simboli, 1971).

At Rabenstein/Corvara massive fluorite precipitated from highly saline (up to 20 wt.% NaCl equiv.) H₂O-NaCl-CaCl₂ solutions at moderate temperatures (Th ≈ 170 °C) and under reducing conditions, as indicated by paragenetic sulphides, the presence of H₂S in fluid inclusions, and the negative Eu anomaly. From their compositions, these solutions correspond to highly evolved formation waters, as reported for other European fluorite vein deposits (e.g. Behr and Gerler, 1987; Jebrak, 1985; Shepherd and Scrivener, 1987; Thomas, 1982). During the deposition of late-stage fluorite, oxidizing conditions prevailed as indicated by sulphate precipitation (trapped bar-

yte) and the disappearance of the negative Eu anomaly. Moreover, secondary inclusions suggest increased mixing of the primary fluid with oxidizing (O²⁻ or SO₄²⁻-rich), lower salinity, and cooler solutions. The latter are assumed to be subsurface waters, which is consistent with the shallow depth of vein formation.

Similar *REE* distribution patterns of fluorites from Brantental/Vallarsa and Prestavel (Fig. 5) suggest fluorite precipitation under similar conditions from a large-scale fluid system. By comparison, the southern deposits of Vignola and Torgola exhibit contrasting patterns, indicating tendencies to mobilization and only a little fractionation (Möller, 1983). These deposits probably contain a remobilized earlier fluorite mineralization.

The source of the fluids responsible for the fluorite vein mineralization in the Bozen area (Fig. 1) must have been very similar. As a 'primary', magmatic fluorite crystallization is excluded, this study favours hydrothermal leaching of the elements during interaction of deep-seated formation waters ('basement brines') with suitable rock units. Fluid ascent was possibly initiated by, but postdated, magmatic activity during the Permo-Triassic rifting of the Southern Alps. The position of the fluorite veins in the vicinity of Late Variscan granitoids and/or Permian acid volcanics is obvious. In this sense, Bakos *et al.* (1972) discuss leaching of fluorine from the Permian 'Bozen quartz porphyries'. Unfortunately the *REE* patterns (Fig. 5c) of these volcanics as well as the basement host-rocks provide no significant information on direct fluorite mobilization. So, the question of the immediate source rock must remain open and requires further detailed investigations.

Conclusions

If a mineral with relatively low hardness and an excellent cleavage, as exemplified by fluorite in this study, is stressed by only weak deformation, its original fluid inclusion content may be altered dramatically or even lost (Bodnar and Bethke, 1984). Thus, there may be limited possibilities of reconstructing conditions of fluorite formation by microthermometry alone. However, combined application of fluid inclusion data and *REE* systematics may permit genetic interpretation of comparable mineralizations on a regional and even transregional scale.

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