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Transport and Deposition of REE in H₂S-rich Fluids: Evidence from Accessory Mineral Assemblages

Transport and deposition of REE in H_2S -rich fluids: evidence from accessory mineral assemblages

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ABSTRACT

It is shown in four examples from geologically different environments that accessory or minor minerals rich in rare-earth elements (REE) are often texturally associated with base-metal sulfides. The examples demonstrate that REE can migrate in hydrothermal fluids containing large amounts of *reduced sulfur* (S^{-II}) species, i.e. H₂S, HS⁻ and S²⁻. In certain fluids complexes of REE with S^{-II} species may be important for the REE transport, but most probably only in the *absence* of other strong ligands such as fluoride, carbonate or possibly phosphate. Textural relationships and geochemical data suggest that the formation of REE-bearing minerals in S^{-II}-rich environments is genetically related to the precipitation of base-metal sulfides.

1. Introduction

Rare-earth element (REE) -rich minerals occupy, like base-metal sulfides, a very special position both from a scientific as well as from an economic point of view. The formation of sulfide minerals was a focus of scientific interest for several generations of geologists, particularly in order to understand the genesis of economically important base-metal sulfide deposits. Elevated concentrations of certain precious metals (e.g., Au, Ag) in some of these deposits has attracted the attention of many mining companies. More recently, detailed investigations have also centered on the geochemical processes leading to the formation of REE deposits, because the REE* gained increasing importance in many different industrial applications (e.g., Morteani, 1991). A relation between REE-minerals and base-metal

sulfides, however, has only rarely been pointed out (e.g., Isokangas, 1978). On the other hand, the close association of REE-minerals with sulfate phases has been known for a long time, because barite, together with carbonate minerals, is the main constituent of one of the largest REE deposits in the world (Mountain Pass, California, U.S.A.; see Olson et al., 1954).

It is the purpose of the present paper to point out mineralogical and textural relationships between REE-bearing accessory minerals and base-metal sulfides in Ti-rich veins from the Adamello Massiv, Italy; these relationships will be compared to observations reported in the literature for two other examples. Moreover, some aspects of REE geochemistry will be addressed in relation to the submarine, H₂S-rich hydrothermal fluids which are commonly found at mid-oceanic ridges. Finally, a tentative geochemical model will be presented offering a possible explanation for the observed association of REE-bearing minerals with sulfides in the Adamello veins.

^{*}The term "REE" includes the lanthanides (La-Lu) as well as Y and Sc, in conformity with the IUPAC rules 1990 (see Leigh, 1990).

2. Titanium-rich veins from Adamello, Italy

Ti-rich veins have been found in the southeastern part of the Adamello contact aureole (Provincia di Trento, northern Italy). The Adamello batholith is the largest igneous complex of Tertiary age in the Alps; it is composed of several petrographically and isotopically distinct plutons (Bianchi et al., 1970) which were intruded into the South Alpine basement and its sedimentary cover between 42 and 30 Ma (Del Moro et al., 1985). The Ti-rich veins occur in graphite-bearing, pure dolomite marbles of upper Triassic age at the contact with a major tonalite intrusion. The presence of the REE-bearing minerals zirconolite (ideally $CaZrTi_2O_7$), aeschynite-(Ce)*, titanite and fluorapatite as accessory or minor phases in these veins provides evidence for mobility of Ti, Zr, REE and actinides (ACT) in a metasomatic fluid (Gieré, 1990a, b).

2.1. Mineralogy

The Ti-rich veins are characterized by four distinct mineral zones, consisting, from margin (oldest part) to center (youngest part), of the following assemblages (Fig. 1):

- (2) pargasite + calcite + titanite + sulfides
- (3) phlogopite + calcite + titanite + sulfides
- (4) titanian clinohumite + spinel + calcite + sulfides

Field relations suggest in combination with petrographic observations that the Ti-rich veins were formed contemporaneously with and outlasted a syn-intrusive deformational event caused by the tonalite emplacement (Gieré, 1990b).

Mineral assemblages and compositions demonstrate that Ti is an important component of the three central vein zones, which are further characterized by the occurrence of accessory minerals rich in REE, ACT and Zr. The three central zones also contain abundant sul-



Fig. 1. Mineralogical map of a hydrothermal vein in contact metamorphic dolomite marble (Do) from the Adamello contact aureole. Ap = apatite; Cc = calcite; Fo = forsterite; Geik = geikielite; Parg = pargasite; Phlog = phlogopite; Rut = rutile; Sp = spinel; Sulf = sulfides; TiCl= titanian clinohumite; Tit = titanite; Zirc = zirconolite. Black areas represent large aggregates of sulfides (mainly pyrrhotite with minor chalcopyrite).

fides (up to ~ 18 vol%), mainly pyrrhotite (with minor chalcopyrite and rare galena). Accessory pyrite occurs exclusively as a secondary mineral in cracks and along grain boundaries of the other sulfides. Textural relationships indicate that pyrrhotite was formed

⁽¹⁾ forsterite + calcite

^{*}A complex REE-Th-Ti-Nb-oxide.



Fig. 2. Photomicrograph showing intergrowth of pargasite and pyrrhotite (*Po*) with enclosed REE-rich fluorapatite (*Ap*). Pargasite zone (sample Br193) from vein shown in Fig. 1. Crossed polarizers, 3.5×2.2 mm.



Fig. 3. Photomicrograph showing intergrowth of REE-rich fluorapatite and pyrrhotite (Po). All rounded grains are fluorapatite. For abbreviations, see Fig. 1. Sample Br196, from vein shown in Fig. 1. Plane polarized light, 3.5×2.2 mm.

contemporaneously with most major (Fig. 2) and accessory minerals (Fig. 3; see also Gieré, 1990b). REE-rich fluorapatite is abundant in all three central zones, and is commonly associated with the Ti-, Zr-, REE- and ACT-bearing minerals (Gieré, 1990a, b) as well as with

the sulfides (Fig. 3). Furthermore, all hydrous minerals, including titanite, contain appreciable amounts of fluorine (Gieré, 1990b, 1992), and thus demonstrate that, besides sulfur and phosphorus, fluorine was an additional constituent of the metasomatic fluid. Another important accessory phase is graphite which occurs in the three central vein zones, but was not found in the forsterite+calcite zone; graphite is also absent in a 1-2-cm-wide zone of *bleached* dolomite marble occurring along the interface between the wall-rock and the outermost vein zone.

Details on the mineralogy of the veins and on the composition of the main minerals may be found in Gieré (1990b). The compositional variation as well as the crystal chemistry of titanite and the accessory REE-bearing minerals have been reported by Gieré (1992) and by Gieré and Williams (1992).

2.2. Whole-rock composition

Whole-rock geochemical data are included here in order to demonstrate the *enrichment in REE* exhibited by the Ti-rich veins relative to the dolomite marble host-rock.

Because it was very difficult to obtain homogeneous aliquots from the different zones due to their coarse-grained appearance and their relatively small width, the data (Tables 1 and 2) are not quantitatively representative for a specific vein zone. This is documented by Fig. 4 (for samples from vein shown in Fig. 1) and by Fig. 5 (for samples from a different vein): while the sample from the titanian clinohumite zone in Fig. 4 is less enriched in REE than the samples from the phlogopite and pargasite zones, the opposite relationship is found in Fig. 5 (cf. also U, Th and Hf contents). Fig. 5 further shows that the phlogopite zone has a relatively variable composition, and therefore, provides additional evidence that a single analysis may not be representative and cannot be used directly for quantitative comparison between samples from the different vein zones. Thus, even if statistically significant differences in REE contents are observed for the analyzed samples, they are not petrographically significant. It is of note, however, that the patterns of all zones are generally parallel. Only samples Br23 and Br149 exhibit a deviation from this trend and are less enriched in light REE (LREE) than the other samples.

The whole-rock data given in Tables 1 and 2 demonstrate that in the three central vein zones REE are present in concentrations up to several hundred ppm (Σ [REE]=77-797 ppm) whereas they commonly are undetectable in the dolomite marble host-rock. This pronounced REE enrichment of the veins relative to the original dolomite marble is clearly emphasized by the chondrite-normalized REE patterns (Fig. 6) which reveal a minimum enrichment of approximately two orders of magnitude for most REE. Fig. 6 further shows that the Ti-rich central vein zones have REE patterns very similar to those found for the nearby tonalite intrusion (data from Gieré, 1990b).

Similarly, the central vein zones are rich in Ti, Zr and ACT (several wt% TiO₂; up to several hundred ppm Zr, U and Th; cf. Tables 1 and 2), whereas these elements are not present or in very small concentrations only in the dolomite marble (TiO₂ < 0.08 wt%, Zr < 16 ppm, $U \approx 6$ ppm, Th < 0.1 ppm). Furthermore, the high sulfur, fluorine and phosphorus contents of the Ti-rich central vein zones (S up to 7 wt%; $F \approx 4000$ ppm, P_2O_5 up to 2.3 wt%) are in sharp contrast to the extremely low concentrations found in the dolomite marble (S < 10)ppm, F = 50-150 ppm, $P_2O_5 = 0.02-0.04$ wt%), and thus document the presence and importance of these components in the metasomatic fluid where they are most probably partly responsible for complexing of high-valence cations (for discussion, see Gieré, 1990a).

In the titanian clinohumite zone relatively high concentrations are also found for Zn, Cr and V (sample Br162; Table 2); these elements are mainly incorporated into the abundant spinel (Gieré, 1990b).

The analytical data discussed above underline the degree of chemical changes produced by the metasomatic fluid during vein formation in the dolomite marble.

TABLE 1

REE and trace-element data (ppm) for Ti-rich vein (shown in Fig. 1) and dolomite marble (determined by instrumental neutron activation analysis)

	Pargasite zone		Phlogopite zone		Titanian clinohumite zone		Graphite-poor dolomite marble	
Sample No.	Br 193	error	Br 194	error	Br 214	error	average ^a (n=5)	error
La	181	±4	208	±4	44.7	±0.8	< 0.5	
Ce	398	±8	399	±8	75	±1	< 0.5	
Nd	165	±6	158	±6	27	± 1	< 0.5	
Sm	23.2	± 0.4	22.6	± 0.4	3.50	±0.06	0.05	± 0.02
Eu	6.85	± 0.08	5.59	± 0.06	0.89	± 0.02	< 0.01	
Gd	n.d.		n.d.		n.d.		< 0.5	
Tb	2.1	±0.1	1.89	± 0.06	0.25	± 0.04	< 0.01	
Tm	n.d.		n.d.		n.d.		< 0.03	
Yb	2.3	±0.2	2.0	±0.2	0.37	± 0.08	< 0.06	
Lu	0.37	± 0.02	0.26	± 0.02	0.07	± 0.02	< 0.04	
$\Sigma(\text{REE})^{b}$	779		797		152		0.05	
Hf	7.2	±0.2	6.9	±0.2	0.08	±0.02	< 0.1	
Th	56	±1	72	±2	< 0.2		< 0.1	
U	17	±2	73	±2	< 0.7		6.1	±0.2

Errors correspond to 2σ errors resulting from counting statistics. For details on analytical technique and samples, see Gieré (1990b).

 $TiO_2 < 0.08$ wt%, Zr < 16 ppm (from X-ray fluorescence analysis; see Gieré, 1990b). Isotope dilution data: Nd=0.176 ppm; Sm=0.0321 ppm.

^bY and Sc not analyzed in samples Br193, Br194 and Br214. For dolomite marble: Y < 6 ppm (from X-ray fluorescence analysis), Sc < 0.1 ppm (from instrumental neutron activation analysis; see Gieré, 1990b).

2.3. Conditions of formation

Thermodynamic analysis of the phase assemblages indicates that the vein minerals crystallized in a relatively water-rich ($X_{CO_2} \approx$ 0.2) environment at a temperature of 500– 600°C and an estimated total pressure of 2000 bar (Gieré, 1990b). The mole fraction of CO₂ was constrained mainly by the titanium phases in the phlogopite zone (rutile, titanite; no perovskite), and thus is theoretically valid for that zone only. The temperatures derived from phase relationships are in good agreement with temperatures calculated from stable isotopic data for coexisting minerals (phlogopite-calcite, pargasite-calcite; for details, see Gieré, 1990b).

Pyrrhotite is the main Fe-bearing mineral in the vein assemblages, and is well suited to study

the relationship between oxygen and sulfur fugacities (f_{O_2}, f_{S_2}) in the fluid. Fig. 7 displays a phase diagram for several phases in the system Fe-Ti-C-O-S, where the pyrrhotite equilibria were calculated with a fixed activity of FeS in pyrrhotite ($a_{\text{FeS}} = 0.425$). This constant activity (value from Barton and Skinner, 1967) is strictly valid only along the pyrrhotite-pyrite equilibrium, because a_{FeS} in pyrrhotite is dependent on the fugacity of S_2 (see Fig. 7). Therefore, the reaction between pyrrhotite and magnetite should be represented by a curve rather than a straight line. In Fig. 7 equilibria between ilmenite and rutile (thin lines) have been superimposed onto the iron oxide-sulfide equilibria. Furthermore, because graphite occurs in the three central vein zones, the reaction:

$$C + O_2 \rightleftharpoons CO_2 \tag{1}$$

TABLE 2

Phlogopite zone Titanian clinohumite zone Sample No. Br 23 Br 149 error Br 157 error Br 162 error error (ppm): 110.0 ± 0.6 La 11.0 ± 0.2 19.3 ±0.2 117.0 ± 0.4 ± 2 Ce 29 ± 1 54 ±1 225 ±2 262 Nd 15 ± 2 32 ±2 94 ± 3 149 ± 6 Sm 4.2 ± 0.2 8.5 ±0.2 16.0 ±0.2 22.8 ± 0.2 0.9 ± 0.1 ± 0.1 2.5 ± 0.1 3.4 ± 0.1 Eu 1.6 7 ± 1 14 ±3 22 ± 3 Gd < 2.5 Tb 0.49 ± 0.04 1.0 ± 0.1 1.3 ± 0.1 2.2 ± 0.1 ± 0.08 n.d. Tm 0.17 n.d. n.d. ± 0.2 ± 0.2 1.7 ±0.2 3.1 ± 0.3 Yb 1.0 1.7 0.3 ± 0.1 0.20 ± 0.02 0.26 ± 0.02 Lu 0.15 ± 0.02 ± 3 ±4 13 ±4 Ya <2 5 10 ±0.4 18.1 21.6 ±0.4 3<u>7.8</u> ± 0.2 Sc 15.3 ±0.6 77 148 503 626 $\Sigma(\text{REE})$ ± 0.2 5.4 ±0.4 Hf 4.5 5.6 ±0.2 ± 0.2 11.1 Ta 1.9 ± 0.2 2.8 ± 0.2 2.5 ± 0.2 5.3 ± 0.2 Th 11 ±1 11 ± 1 52 ±4 105 ± 12 ± 2 38 ± 1 67 ±1 33 130 ±4 U Cs 12.6 ± 0.4 11.4 ± 0.6 10.0 ± 0.6 < 0.6 176 142 ± 12 151 ± 12 16 ±6 Rb^a ± 10 354 ± 30 461 ± 54 156 ± 54 Ni^a 229 ± 40 44.5 ± 0.6 72.0 ± 0.8 86.4 ± 0.8 19.4 ±0.4 Co^a ± 19 ± 23 14 ±3 Cu^a 676 1.153 3,251 ± 11 94 93 ± 8 ±16 4,769 ± 100 Znª ± 8 638 Crª 323 ±6 350 ± 8 580 ± 10 1,261 ± 30 Fb 4,152 ± 200 3,915 ± 200 4,612 ± 200 4,697 ± 200 393 Zrª 125 ± 12 151 ±12 195 ±12 ±12 Vª 471 ± 11 384 ± 10 357 ±11 755 ±15 (wt%): Sa 0.02 ± 0.01 4.19 ± 0.03 6.95 ± 0.05 5.85 ± 0.04 ± 0.03 4,47 ± 0.03 TiO₂ª 2.11 ± 0.02 2.51 ± 0.03 2.51

REE and trace-element data for samples from Ti-rich veins (data determined by instrumental neutron activation analysis unless stated otherwise)

Errors correspond to 2σ errors resulting from counting statistics. For details on analytical techniques and samples, see Gieré (1990b).

^aFrom X-ray fluorescence analysis.

^bFrom ion selective electrode potentiometry.

has been plotted into the diagram; it is represented by a thick solid horizontal line for $X_{CO_2} = 1.0$, and by a dashed horizontal line for $X_{CO_2} = 0.2$. The latter corresponds to the mole fraction of CO₂ inferred from the Fe-free silicate-oxide assemblages in the phlogopite zone. The graphite and ilmenite equilibria were calculated because magnesian ilmenite was found to coexist with graphite in the phlogopite zone of the vein shown in Fig. 1 (Gieré, 1990b). No quantitative microprobe data are available for that particular ilmenite; thus, the equilibria



Fig. 4. Chondrite-normalized REE patterns for the three Ti-rich central zones of the hydrothermal vein shown in Fig. 1. Chondrite values from Wakita et al. (1971). Error bars represent 2σ errors due to counting statistics (data from instrumental neutron activation analysis, see Table 1). Sample numbers in *brackets*.

were calculated for unit activity (solid lines) as well as for an ilmenite activity of 0.5 (dashed lines). As shown in Fig. 7, reaction (1) at $X_{CO2} = 0.2$ intersects the ilmenite-rutile reaction with $a_{FeTiO3} = 0.5$ at a sulfur activity of $\sim 10^{-7}$. From Fig. 7 it was thus concluded that the fluid had the activities $a_{O2} = 10^{-23.5}$ and $a_{S2} = 10^{-7}$ (at T = 600 °C and $P_{tot} = 2000$ bar) during formation of the sulfide-bearing vein zones (at least during formation of the phlogopite zone), which at the same time are the vein zones containing the REE-, ACT-, Ti- and Zr-rich minerals.

These results, combined with thermodynamic data for the three equilibria:

 $H_2 + 0.5O_2 \rightleftharpoons H_2O \tag{2}$

$$\mathbf{H}_2 + 0.5\mathbf{S}_2 \rightleftharpoons \mathbf{H}_2\mathbf{S} \tag{3}$$

$$O_2 + 0.5S_2 \rightleftharpoons SO_2 \tag{4}$$



Fig. 5. Chondrite-normalized REE patterns for four samples from hydrothermal Ti-rich veins very similar to the one shown in Fig. 1. Chondrite values from Wakita et al. (1971). Error bars represent 2σ errors due to counting statistics (data from instrumental neutron activation analysis, see Table 2). Sample numbers in *brackets*.

and with experimental data on the partitioning of F and Cl between apatite and fluid (Korzhinskiy, 1981), allowed the fugacities of several species in the metasomatic fluid to be calculated (for details, see Gieré, 1990b). The results are listed in Table 3, and show that H₂S was the dominant sulfur species in the fluid $(f_{H_{2S}}: f_{S_{2}}: f_{SO_{2}} \approx 10^{6}: 0.6: 1)$, implying a rather low pH. As shown by Ohmoto (1972), sulfides precipitating in the H₂S predominant field exhibit δ^{34} S isotopic compositions similar to the total δ^{34} S composition of the fluid. Thus, the sulfur isotope data given by Gieré and Hoering (1990) can be used as indicators for the source of the sulfur. The sulfur isotope data confirm the conclusions drawn from other stable isotope data (Gieré, 1990b) as well as from radiogenic isotope data (Gieré et al., 1988; Gieré, 1990b), suggesting that the Ti-rich veins were formed from a magmatic, most probably ton-



Fig. 6. Chondrite-normalized REE patterns displaying the compositional ranges for the Ti-rich veins (*shaded*, from Figs. 4 and 5), for the tonalite intrusion (*black*, data from Gieré, 1990b), and for the dolomite marble (*stippled*; *full squares*= graphite-rich sample, data from instrumental neutron activation analyis; *full circles*=graphite-poor sample, data from isotope dilution analysis; cf. Gieré, 1990b). Open triangles represent the detection limit for the instrumental neutron activation analysis of the dolomite marble samples. Chondrite values from Wakita et al. (1971).

alitic fluid which was diluted (by $\sim 50\%$) by a fluid derived from the adjacent dolomite marble.

3. Comparison with other examples

Described below are two examples from geologically different environments; they show textural features which are similar to those found in the Adamello veins, and their mineral assemblages infer that the REE have been transported by a fluid rich in reduced sulfur.

3.1. Zirkelite-jordisite veins (former U.S.S.R.)

Rekharskiy and Rekharskaya (1969) discovered a zirkelite^{*}-jordisite (MoS_2) vein assemblage in zones of altered volcanic rocks.



Fig. 7. Phase diagram for iron and sulfur phases with superimposed graphite- CO_2 equilibrium. Pyrrhotite stability field is *stippled*. The diagram was calculated for a fixed activity of FeS in pyrrhotite ($a_{FeS}=0.425$) using the GEO-CALC software package (Brown et al., 1988). Thermodynamic data for pyrite and troilite from Robie et al. (1979), for all other phases from Berman (1988). Arrow indicates the direction of increasing FeS activity in pyrrhotite. Abbreviations: Hm=hematite; Mt=magnetite; Po=pyrrhotite; Py=pyrite; Ilm=ilmenite; Rut=rutile. Dashed lines are for X_{CO2} =0.2 (thick horizontal line) and a_{FeTIO3} =0.5 (thin lines). Black dot shows approximate conditions of vein formation. See text for discussion.

The fresh volcanic rocks of trachytic to rhyolitic composition consist mainly of plagioclase, potassium feldspar, biotite and quartz, and contain accessory titanite, zircon and magnetite. Hydrothermal alteration transformed the original magmatic assemblage into kaolinite+quartz or sericite+quartz, and led to the formation of veins and stringers of zirkelite+jordisite within the highly altered zones.

Zirkelite and jordisite are intimately inter-

^{*}Like zirconolite a polymorph of the compound $CaZrTi_2O_7$.

TABLE 3

Logarithmic values of fugacities (bar) of selected species in the vein-forming fluid at Adamello

3.0	
3.3	
-20.0	
0.9	
- 5.0	
-4.8	
1.2	
-2.1	
-1.1	
	$3.0 \\ 3.3 \\ -20.0 \\ 0.9 \\ -5.0 \\ -4.8 \\ 1.2 \\ -2.1 \\ -1.1$

Calculated for T=600 °C, $P_{tot}=2000$ bar and $X_{CO2}=0.2$ (corresponding to the mole fraction of CO₂ inferred from the mineral assemblage in the phlogopite zone).

grown with each other as well as with abundant metasomatic pyrite which occurs in microgranular aggregates or as idiomorphic crystals. No other minerals have been described from the vein assemblage. Chemical analyses showed that these veins, besides being rich in REE, also contain elevated concentrations of U, Hf and Nb, as well as Pb, Zn, As, Sb, Cu and Ag (concentrations unspecified by the authors).

Based on the genetic relation between the mineral association in the veins and the host rocks, Rekharskiy and Rekharskaya (1969) concluded that the vein minerals were formed presumably at temperatures of $\sim 100-200$ °C. The mineral assemblage further suggests that sulfur was an important component in the metasomatic fluid. The mineral assemblage does not provide any evidence for the presence of other fluid components (e.g., F, P) which seem to be important for the transport of REE in the Adamello example. The intergrowth of a REE mineral with a sulfide mineral, however, is characteristic of both examples.

3.2. Galena mine at Korsnäs (Finland)

The Korsnäs lead deposit, also known as Svartören deposit, occurs in a large vertical fracture which cuts the foliation of the local migmatitic gneisses of the Svecofennian schist belt. As reported by Isokangas (1978), the fracture-filling vein consists mainly of galena, calcite, microcline, diopside and scapolite, and grades laterally into a pegmatite. Galena forms massive aggregates up to several meters in diameter and is the most important sulfide in the deposit (minor amounts of sphalerite, molybdenite, pyrrhotite, pyrite, chalcopyrite). A REE concentrate was generated as a by-product of galena mining at Korsnäs. The high REE contents of the ore (0.91 wt% REE₂O₃) are due to the presence of abundant apatite and monazite which both tend to be associated with galena.

Although the formation of this deposit is not well understood (see Isokangas, 1978), the textural association of the REE-bearing phosphates with galena is characteristic and could indicate a mutual genetic relationship. Because scapolite can incorporate significant amounts of sulfur, chlorine and CO_2 , its presence in the paragenesis suggests that the veinforming process may have involved, besides sulfur and phosphorus, also chlorine and CO_2 , the latter additionally documented by the abundance of calcite.

4. Submarine hydrothermal vent fluids

Since the discovery of submarine hydrothermal venting ("black smokers") on the East Pacific Rise (Macdonald et al., 1980; Spiess et al., 1980), considerable efforts have been made to analyze the chemical composition of the hydrothermal fluids which, blackened by basemetal sulfide precipitates, are jetting out (several m s⁻¹) from chimneys at temperatures around 350°C, and which are involved at present in the formation of volcanogenic massive sulfide deposits (for comprehensive reviews, see, e.g., Lydon, 1988a, b; Scott, 1991).

The hydrothermal vent fluids are essentially seawater which has been heated and chemically modified by reaction with hot rocks (usually tholeiitic basalts at mid-ocean ridges) a few kilometers below the sea floor, in the socalled high-temperature reaction zone (ancient reaction zone exposed on Cyprus; see Schiffman and Smith, 1988). At sedimentstarved, mid-ocean ridge axes the vent fluids are reducing, H_2S -rich ($H_2S \approx 250$ ppm), mainly acid (pH ≈ 3.5) and, relative to seawater, greatly enriched in a number of metals, particularly Fe, Mn, Cu, Zn; the salinities of the fluids are variable, but commonly near that of seawater resulting in chloride being the main anion (Michard et al., 1984; Von Damm et al., 1985). Fig. 8 shows that the submarine hydrothermal solutions also exhibit a pronounced



Fig. 8. Chondrite-normalized REE patterns showing the ranges in composition of seawater at depths > 1800 m (data from Goldberg et al., 1963; Høgdahl et al., 1968; Elderfield and Greaves, 1982; Klinkhammer et al., 1983; Michard and Albarède, 1986; Greaves et al., 1991), of hydrothermal vent fluids from the East Pacific Rise (Michard et al., 1983; Michard and Albarède, 1986), of volcanogenic massive sulfide deposits (ancient: Graf, 1977; Whitford et al., 1988 — modern: Barrett et al., 1990), and of ochres from Cyprus (Robertson and Fleet, 1976). The REE pattern of a typical mid-ocean ridge basalt is plotted for comparison (*thick solid line* = data from Ludden and Thompson, 1979). Chondrite values from Wakita et al. (1971).

enrichment in *REE* relative to seawater^{*}. This REE enrichment must be ascribed to leaching from the tholeiitic basalts in the high-temperature reaction zone, unless the fluids contain a significant third component (e.g., derived from the mantle). Such a component, however, is not readily detected in these fluids, although some indications exist (Lupton et al., 1980; Michard et al., 1984; Michard and Albarède, 1986). As demonstrated by Ludden and Thompson (1979), substantial amounts of REE can be mobilized during the seawater-basalt interaction which also releases the sulfideforming metals into the fluid (cf. Humphris and Thompson, 1978a, b; Mottl and Holland, 1978; Reed, 1983). Comparison of the REE patterns of a typical mid-ocean ridge basalt with those of the vent fluids (Fig. 8) suggests that the LREE (and in particular Eu) preferentially fractionate into the fluid during the seawater-basalt interaction. These data show that at elevated temperatures acid solutions are able to transport high amounts of ore-forming metals along with *REE* in the presence of large excesses of H_2S .

Both ancient and recent volcanogenic massive sulfide deposits have extremely variable REE contents (cf. Graf, 1977; Alt, 1988; Whitford et al., 1988; Barrett et al., 1990); generally, however, they are distinctly richer in REE than the modern vent fluids (Fig. 8), indicating that the REE are trapped during precipitation of the base-metal sulfides. The sulfides are precipitated when the ascending fluids are discharged into the ambient seawater; thus, the upper part of a "black smoker" sulfide chimney is the most likely place for deposition of REE. In terms of the minerals in which the REE

^{*}The REE data for seawater include samples from depths > 1800 m only, i.e. where most hydrothermal activity takes place, because the REE content of seawater generally increases with depth (e.g., Goldberg et al., 1963; Elderfield and Greaves, 1982; Klinkhammer et al., 1983; De Baar et al., 1985), and because it may be influenced at shallower levels by other factors (e.g., REE-rich Mediterranean outflow in the North Atlantic; see Greaves et al., 1991).

are accommodated, Morgan and Wandless (1980) have shown that REE are not readily incorporated into galena; by analogy, other sulfides are also likely to be REE-poor. Morgan and Wandless (1980), however, demonstrated that anhydrite, a prominent mineral in "black smoker" sulfide chimneys (Haymon and Kastner, 1981; Haymon, 1983; Graham et al., 1988), accommodates rather high amounts of REE (particularly LREE). This was also confirmed by Michard and Albarède (1986) who found relatively high REE concentrations in anhydrite from the East Pacific Rise.

Fe-rich, Mn-depleted sediments, known as ochres, occur above some ancient sulfide orebodies on Cyprus and are the products of in situ submarine sulfide oxidation (Robertson and Fleet, 1976); they tend to be enriched in many REE relative to the massive sulfide deposits shown in Fig. 8. A similar relationship has been observed for modern submarine gossans from a hydrothermal field on the Mid-Atlantic Ridge (Trans-Atlantic Geotraverse; cf. Hannington et al., 1991). In some cases, thus, oxidation of sulfide orebodies seems to further increase their REE contents, but it involves, like the formation of hydrothermal metalliferous sediments, an additional REE component due to adsorption of seawater-derived REE onto Fe-oxyhydroxides (Barrett et al., 1988; Hannington et al., 1991; Mills et al., 1991).

5. Discussion

The above examples demonstrate that at elevated temperatures H_2S -rich fluids are very effective in transporting large amounts of oreforming base metals as well as lesser, but nonetheless significant quantities of REE and other elements (in some cases ACT, Ti, Zr). The mineralogical, geochemical and textural relationships described for the Adamello veins and summarized for the other examples suggest that the REE are trapped at the site of sulfide precipitation. At these sites, however, the REE are not incorporated into sulfide minerals (Morgan and Wandless, 1980), but rather into accessory or minor phases with a high affinity for REE [i.e. monazite, aeschynite, zirconolite/zirkelite, apatite and titanite; in submarine assemblages: barite (Barrett et al., 1990), and anhydrite]. All these minerals are texturally closely associated with the sulfides (Figs. 2 and 3; see also Haymon, 1983; Gieré, 1990b, 1992; Gieré and Williams, 1992), indicating that the deposition of REE from the hydrothermal fluids could be genetically related to the crystallization of base-metal sulfides.

5.1. Transport of REE

The presence of large amounts of H_2S in certain hydrothermal fluids suggests that under these special conditions the REE might form complexes with reduced sulfur (S^{-II}) species, i.e. H_2S , HS^- and S^{2-} . The possible role of S^{-II} complexes in transporting REE has also been pointed out by Wilton (1985). To the author's knowledge, however, no experimental data exist on complex formation of sulfide species with **REE-sulfides** REE, although crystalline (REE_2S_3) are known in the laboratory (Flahout, 1979). In contrast to this, experimental data and theoretical predictions suggest that sulfate ions form relatively strong complexes with REE (cf. Wood, 1990). Moreover, sulfate complexes, could be important even if the concentration of reduced sulfur in the fluid is larger than that of sulfate. Hot vent fluids from the East Pacific Rise, for example, contain only approximately one order of magnitude more H_2S than SO_4^{2-} (end-member concentrations; see Von Damm et al., 1985); therefore, sulfate complexes could be more important, if the stability constants for the REE-sulfate complexes are more than an order of magnitude greater than those for REE-sulfide complexes.

The mineral assemblage in the zirkelite-jordisite veins does not point to the presence in the fluid of complexing agents other than a reduced sulfur species or possibly hydroxide ions. In this particular case, OH^- and S^{-II} species are the most likely ligands for complexing and transporting the REE in the hydrothermal fluid which also carried Fe, Mo, U, Ti and Zr. Agapova et al. (1989) demonstrated that the solubility of anatase increases with increasing contents of total reduced sulfur in hot sulfidecarbonate solutions (200°C, 100 atm; constant pH of intermediate value); from these results they concluded that Ti forms mixed-ligand bisulfide-carbonate-hydroxide complexes. Since Ti is a prominent metal in the REE-rich zirkelite-jordisite veins and often behaves similarly to the REE in hydrothermal fluids (Gieré, 1990a), the experiments of Agapova et al. (1989) contribute to understanding the formation of these veins, particularly because the studied solutions appear to be very effective also in transporting Mo and U (Agapova et al., 1987).

The above example indicates that REE-S^{-II} complexes might be of considerable importance in hydrothermal fluids, but most probably only in the absence of other potentially strong ligands (see also Brookins, 1989). If strong complex-forming ligands such as fluoride, carbonate or possibly phosphate are present, the suggested S^{-II} complexes with REE would probably not be important because of the strong affinity of the hard REE ions for oxygen donors from hard ligands, especially at higher temperatures (Ahrland, 1968; Nancollas, 1970). In the Adamello example the veinforming fluid contained elevated concentrations of the hard ligands fluoride and phosphate, which thus are the most likely ligands for complexing the REE (cf. Gieré, 1990a, b, 1992). Similarly, the suggested REE-S^{-II} complexes probably play only a minor role in the submarine hydrothermal vent fluids where chloride is the main anion.

5.2. Mechanisms of REE deposition

If REE-S^{-II} complexes do exist, crystallization of sulfide minerals might cause precipitation of REE. This mechanism can be illustrated by considering the equations:

 $\operatorname{REE}(\operatorname{HS})_{3}^{0} \rightleftharpoons \operatorname{REE}(\operatorname{HS})_{2}^{+} + \operatorname{HS}^{-}$ (5)

$$\operatorname{REE}(\operatorname{HS})_2^+ \rightleftharpoons \operatorname{REE}(\operatorname{HS})^{2+} + \operatorname{HS}^- \tag{6}$$

$$\operatorname{REE}(\operatorname{HS})^{2+} \rightleftharpoons \operatorname{REE}^{3+} + \operatorname{HS}^{-}$$
(7)

which describe three possible complexation equilibria of trivalent REE ions with bisulfide ligands. In high-temperature fluids, where metal ions tend to form neutral complexes (Seward, 1981; Crerar et al., 1985), the removal of large amounts of reduced sulfur due to precipitation of sulfide minerals, thus, would lead to the stepwise breakdown of the neutral REE(HS)⁰₃ complexes, and eventually to the formation of REE³⁺ ions which then might be deposited in REE-bearing phases.

A similar model has been proposed by Gieré (1990a) in order to explain textural relationships between the F-rich and the REE-, Ti- and Zr-bearing minerals in the Adamello veins. This suggestion is based on and indirectly supported by experimental results as well as by theoretical considerations, which demonstrate that fluoride is a very effective ligand for complexing of REE, at least in the intermediate pH region and at temperatures up to 350°C (Wood, 1990). Thus, a decrease in the fluoride activity, caused, for example, by the crystallization of fluorapatite or F-rich silicates, might induce breakdown of the REE-fluoride complexes. Similarly, Kosterin (1959) suggested that crystallization of calcite or dolomite in hydrothermal systems leads to a decrease in the CO_3^{2-} concentration in the fluid, resulting in a breakdown of the REE-carbonate complexes. The latter can be important for the transport of REE in near-neutral to basic hydrothermal fluids (Wood, 1990).

The suggested genetic relationship between base-metal sulfides and REE-bearing minerals, however, is probably more complex in cases where both S^{-II} species and stronger complex-forming ligands are present in the fluids (e.g., Adamello, vent fluids). The removal of large amounts of reduced sulfur by crystallization of sulfide minerals, thus, would not directly affect the stability of complexes like, for example, REEF_3^0 or $\text{REE}(\text{PO}_4)^0$, but it may significantly change other fluid properties, e.g. pH or Eh, which in turn could induce deposition of REE.

This mechanism is best illustrated by considering chloride-rich hydrothermal fluids in which ore-forming elements such as Fe, Cu, Zn or Pb are carried as chloride complexes (e.g., Barnes, 1979). Sulfide precipitation from these particular fluids can be described by the general reaction:

$$\operatorname{MeCl}_{2}^{0} + \operatorname{H}_{2}S \rightleftharpoons \operatorname{MeS}_{2} + 2\operatorname{H}^{+}_{+} + 2\operatorname{Cl}^{-}_{(\text{sulfide})}$$
(8)

which may be formulated, for example, for pyrrhotite, pyrite, sphalerite or galena, but also for chalcopyrite (Eugster, 1985, 1986). This conversion of metal chloride solutes to sulfide minerals is liberating H⁺ (or HCl) which increases the acidity of the hydrothermal fluid. Deposition of the dissolved REE might then occur *in response* to such a change in pH, induced by crystallization of the sulfide minerals, rather than as a consequence of the breakdown of REE-S^{-II} complexes.

Evidence for this type of mechanism is provided, for example, by the hydrothermal vent fluids: dramatically different conditions are encountered suddenly by the hot $(T \approx 350^{\circ} \text{C})$, acid (pH \approx 3.5), H₂S- and chloride-rich, REE-bearing vent fluids at the seafloor when they are ejected into the cold $(T \approx 2^{\circ}C)$, alkaline (pH \approx 8) and SO₄²⁻-rich seawater; this is leading to immediate precipitation of sulfide minerals. It seems that most REE dissolved in the hydrothermal fluids are deposited at the site of sulfide precipitation; this is suggested by the REE patterns of hydrothermal metalliferous sediments *further away* from the vent sites which indicate that the REE deposited in such distal sites are mainly derived from seawater (e.g., Barrett et al., 1988). Besides being incorporated into anhydrite (see p.261), the REE could further be removed from the vent fluids by adsorption onto the surface of the precipitating sulfide minerals*.

5.3. Sulfide precipitation and REE deposition in the Adamello veins

The aspects of REE transport and deposition outlined above can be combined into a *tentative model* in order to explain the interdependence between the formation of sulfides and the crystallization of REE-bearing minerals in the Adamello veins.

As mentioned above (p.257), the isotopic data suggest that the vein-forming fluids were derived from the nearby tonalite intrusion, representing fluids which probably separated from the tonalitic melt during emplacement of the tonalite (Gieré, 1990b). Such fluids are expected to be acid and relatively oxidizing (judging from the silicate assemblage in the Adamello tonalite probably in the range of 1-2 log units above FMQ; see Frost and Lindsley, 1992). A relatively oxidizing original fluid is also indicated by the average sulfur isotope composition of the veins as well as by the oxidation state of sulfur in the tonalite, where sulfur appears to be mainly contained in apatite, probably as sulfate substituting for phosphate (Gieré and Hoering, 1990).

This tonalitic fluid then interacted with the dolomite marble causing oxidation of the wall-rock graphite [according to reaction (1)] in the immediate vicinity of the veins (bleached dolomite marble; see p.254), and producing the graphite-free assemblage forster-ite+calcite (Fig. 1). Formation of this vein zone may be expressed as

$$2\operatorname{CaMg}(\operatorname{CO}_3)_2 + \operatorname{SiO}_{2(\operatorname{aq})} \rightleftharpoons \operatorname{dolomite})$$

$$2CaCO_3 + Mg_2SiO_4 + 2CO_2$$
(9)
(calcite) (forsterite)

^{*}The REE are known to be rapidly adsorbed, for example, onto Fe-oxyhydroxides (Byrne and Kim, 1990; Koeppenkastrop and De Carlo, 1992).

This decarbonation reaction leads to a *dilu*tion of the metasomatic fluid which is consistent with the stable isotopic data indicating that the original fluid was diluted by dolomite-derived components (Gieré, 1990b). As pointed out by Crerar and Barnes (1976) and Barnes (1979), dilution of fluids carrying ore-forming elements may induce precipitation of sulfide minerals, because the activity of ligandforming anions (e.g., Cl^{-}) is decreased. This conclusion is drawn from reactions similar to reaction (8) which could be representative for precipitation of the sulfides in the Adamello veins. Reaction (8) assumes that the oreforming metals are transported as chloride complexes, which is feasible for the Adamello example because of the relatively high fugacity of HCl⁰ in the fluid (Table 3).

The general sulfide-forming reaction (8), probably initiated by fluid dilution due to progression of reaction (9), would lead to an increase in the *fluid acidity*. In carbonate rocks this acidity is generally neutralized by calcite dissolution and production of a CaCl⁰₂ brine (Kwak and Tan, 1981; Eugster, 1985) according to the schematic reaction:

 $CaCO_3 + 2H^+ + 2Cl^- \rightleftharpoons CaCl_2^0 + CO_2 + H_2O \qquad (10)$ (calcite)

In high-temperature, relatively reducing fluids Cu is mainly transported as $CuCl^{0}$ (Crerar and Barnes, 1976), while Fe commonly forms $FeCl_{2}^{0}$ complexes (Chou and Eugster, 1977; Crerar et al., 1985). Combining this information with reactions (8) and (10) leads to the chalcopyrite-forming model reaction:

 $3CaCO_3 + 4H_2S + 2CuCl^0 + 2FeCl_2^0 \Rightarrow$

 $2CuFeS_2 + 3H_2O + 3CaCl_2^0 + 3CO_2 + H_2$ (chalcopyrite)

(11)

or, expressed in a different way,

 $6CaCO_3 + 8H_2S + 4CuCl^0 + 4FeCl_2^0 \rightleftharpoons$

$$\begin{array}{l} 4CuFeS_2 + 8H_2O + 6CaCl_2^0 + 5CO_2 + C\\ \text{(chalcopyrite)} & \text{(graphite)} \end{array}$$

(12)

These reactions, both involving oxidation of Cu^+ to Cu^{2+} , could describe the precipitation of chalcopyrite in the Adamello veins. Furthermore, reaction (12) leads to the formation of graphite and therefore, would explain why both graphite and chalcopyrite occur in the three central Ti-rich assemblages. Reactions (11) and (12) could both eventually shift the oxygen fugacity of the fluid to values lower than those of the original fluid derived from the intrusion, permitting the precipitation of pyrrhotite (cf. Fig. 7). Pyrrhotite formation can readily be described by reaction (8); the resulting decrease in pH could then induce the breakdown of REE complexes. This breakdown may be expressed, for example, as:

$$\operatorname{REE}(\operatorname{PO}_4)^0 + 3\mathrm{H}^+ \rightleftharpoons \operatorname{REE}^{3+} + \mathrm{H}_3\mathrm{PO}_4^0 \quad (13)$$

or

(apatite)

 $REEF_3^0 + 3H^+ \rightleftharpoons REE^{3+} + 3HF^0$ (14)

for the case of a complete, three-step breakdown of possible phosphate or fluoride complexes to trivalent REE ions. Moreover, crystallization of apatite, formulated schematically as:

$$5CaCO_3 + 3H_3PO_4^0 + HF^0 \rightleftharpoons$$
(calcite)
$$Ca_5(PO_4)_3F + 5CO_2 + 5H_2O$$
(15)

would further aid in *destabilizing* the inferred REE complexes. Reaction (15) could also explain the close textural association of fluorapatite with the REE-bearing minerals (Gieré, 1990a; Gieré and Williams, 1992).

Reactions (11), (12) and (15) may also be formulated in terms of *dolomite dissolution*: the formation of chalcopyrite could then be written as*:

^{*}Formulated in such a way as to exclude formation of magnesite, because magnesite was not observed in the apatite-bearing vein zones.

$$6CaMg(CO_3)_2 + 8H_2S$$
(dolomite)
$$+4CuCl^0 + 4FeCl_2^0 + 12HCl^0 \rightleftharpoons$$

$$4CuFeS_2 + 14H_2O + 6CaCl_2^0 + 6MgCl_2^0$$
(chalcopyrite)
$$+11CO_2 + C$$
(graphite)
(16)

whereas apatite formation could be described as:

$$5CaMg(CO_{3})_{2} + 3H_{3}PO_{4}^{0} + HF^{0} + 10HCl^{0} \rightleftharpoons$$
(dolomite)
$$Ca_{5}(PO_{4})_{3}F + 5MgCl_{2}^{0} + 10CO_{2} + 10H_{2}O$$
(17)
(apatite)

It has to be stressed, however, that neither apatite nor chalcopyrite were found in the forsterite+calcite zone, the only vein zone in contact with the dolomite marble wall-rock (Fig. 1). This is suggesting that the formation of both chalcopyrite and apatite implies the presence of calcite rather than dolomite, a condition which is met by the metasomatic fluid only *after* formation of the forsterite+calcite assemblage. Therefore, reactions (12) and (15) best describe the crystallization of chalcopyrite and apatite.

Similarly, according to the model presented above, the calcite crystals present in each of the sulfide-bearing assemblages (Fig. 1) could have been formed only *after* neutralization of the acidity produced by sulfide precipitation and after crystallization of apatite. An early crystallization of apatite within the sulfidebearing, Ti-Zr-, REE- and ACT-rich vein zones is also indicated by the euhedral shape of most apatite crystals.

This tentative model could explain the observed mineralogical zoning with respect to some of the minerals present in the Adamello veins. Clearly, the model has to be elaborated in more detail in order to understand the zoning also with respect to pargasite, phlogopite, titanian clinohumite and spinel (R. Gieré, in prep.).

6. Summary

As shown in this study, the REE can be transported by reducing, H₂S-rich fluids in a wide range of different geological environments. Complexes of REE with S^{-II} species may be important in certain hydrothermal fluids, but most probably only in the absence of other strong ligands such as fluoride, carbonate, or possibly phosphate. In the environments described above, textural relationships and geochemical data suggest that the formation of REE-bearing accessory and minor minerals appears to be genetically linked to the precipitation of base-metal sulfides. Two different kinds of mechanisms for REE deposition can be envisaged both producing similar, possibly indistinguishable textures:

(1) The precipitation of sulfides could induce REE deposition by the removal of S^{-II} species and concomitant breakdown of the REE- S^{-II} complexes.

(2) If the REE are complexed in the fluid by other, stronger ligands, the breakdown of such REE complexes (e.g., REEF_3^0) could be a response to *changes in fluid properties*, such as pH or Eh induced by crystallization of sulfide minerals.

The mechanisms proposed here could both explain the observed trapping of REE at the site of sulfide precipitation. The Adamello veins provide a good example for the complex interdependence between crystallization of sulfide minerals, changes in fluid composition, and the deposition of REE.

Base-metal sulfide deposits may contain appreciable amounts of REE; they can be further enriched in REE when affected by secondary processes as documented, for example, by oxidation of submarine sulfide orebodies. This could indicate that under certain circumstances, sulfide deposits might become potential REE deposits.

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