ORIGIN AND DISTRIBUTION OF SOME TRACE ELEMENTS IN METAMORPHOSED Fe–Mn DEPOSITS, VAL FERRERA, EASTERN SWISS ALPS

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ABSTRACT

Numerous small Fe–Mn deposits occur in Triassic marbles of the Middle Penninic Suretta, Starlera, and Schams nappes in Val Ferrera, eastern Swiss Alps. These deposits are characterized by high contents of Ba, Sb, As, V, Be, W, and rare-earth elements (REE), and most likely represent chemical sediments deposited around submarine springs, similar to some modern seafloor metalliferous sediments. Circulation of the hydrothermal fluid within the granite-bearing basement underlying the sedimentary rocks is inferred as the most likely mechanism for the derivation of the Be and W concentrated in the ores. The orebodies studied shared a similar Alpine metamorphic evolution, culminating with blueschist- to greenschist-facies conditions. The chemical and mineralogical composition of the ores strongly influenced the behavior of the minor constituents Ba, Sr, Sb, As, V, Be, W, and REE. During the main deformation (D1), As and V, for example, were incorporated into hematite in Fe-rich ores, whereas in Mn-rich ores they were concentrated into accessory minerals growing in the main schistosity. These syn-D1 minerals represent important sinks of trace elements released by recrystallization or breakdown of their primary hosts as a result of prograde metamorphism. Post-D1 mobility of Ba, Sb, As, V, Be, REE and, in some cases, W is recorded by various mineral parageneses that either overgrow the S1 schistosity or occur in several types of discordant veins. In addition to the chemical and mineralogical controls, the structural position of the deposit influenced the remobilization of trace elements. Element mobility during the Alpine greenschist-facies metamorphism within the Fe–Mn ores involved large-ion lithophile elements (Be, Sr, Ba), high-field-strength elements (Mo, W, Sb, As), and the light REE. The geochemical signature is analogous in many respects to the remobilization observed during subduction-related metamorphism and during metasomatism in the mantle.

Keywords: exhalative Fe–Mn ores, metamorphism, paragenetic evolution, geochemistry, rare-earth elements, Val Ferrera, Swiss Alps.
Mott-clés: minerais Fe–Mn exhalatifs, métamorphisme, évolution paragénétique, géochimie, terres rares, Val Ferrera, Alpes Suisses.

INTRODUCTION

Manganese deposits metamorphosed under low- to high-grade conditions have furnished a large number of unusual minerals containing Sb, As, V, Be, W, the light rare-earth elements (LREE), Ba, and Sr. For example, minerals of Sb, As, and V have been observed, locally in relatively large quantities, in radiolarite-hosted deposits at Falotta in the Oberhalbstein, Switzerland (Geiger 1948), at Praborna in the Aosta Valley, Italy (Martin–Vernizzi 1984, Perseil 1991), and in the Ligurian Alps, Italy (Cortesogno et al. 1979), in other chert-hosted deposits in the Hautes-Pyrénées in France (Ragu 1990, 1994) and at Madhya Pradesh, India (Ostwald & Nayak 1993), in sandstone-hosted deposits at the Kombat mine, Namibia (Dunn 1991); and in carbonate-hosted deposits at Franklin, New Jersey (Dunn 1995) and in Sweden and Norway (Långban-type deposits, Boström et al. 1979, Holtstam et al. 1998). Beryllium minerals, on the other hand, are reported from Långban (Sweden), Hautes-Pyrénées, Franklin (Essene & Peacor 1987), and Falotta (Graeser 1995), whereas W and LREE minerals were found at Långban, Hautes-Pyrénées, and Franklin. Finally, Ba and Sr minerals (mostly strotian barite) are present in all of the deposits mentioned above. A syngenetic exhalative origin has been inferred for all of these deposits. The timing of the enrichment in Sb, As, V, Be, W, LREE, Ba, and Sr, however, is not always clear because the minerals incorporating these elements occur mostly in late veins that postdate the peak of metamorphism.

Arsenic is typically enriched in synsedimentary Fe–Mn deposits (Pfeiffer et al. 1988). Beryllium and W, on the other hand, are commonly associated with granitic rocks (Guilbert & Park 1986), and their occurrence in late veins within syngenetic Fe–Mn deposits has in some cases been interpreted as indicating chemical input from post-ore granitic intrusions (e.g., Ragu 1990, 1994). In general, very little is known about the mobilization history of Sb, As, V, Be, W, REE, Ba, and Sr within metamorphosed Fe–Mn deposits in the time span between metamorphic climax and formation of the late veins, because geochemical studies aim to reconstitute the pre-metamorphic state, and mineralogical studies are mostly concerned with crystal–chemical features of the rare minerals rather than with genetic aspects.

We describe in this paper mineral assemblages recently discovered in four genetically related carbonate-hosted stratiform metamorphosed Fe–Mn deposits in Val Ferrera, eastern Central Alps, Switzerland. We present whole-rock geochemical data for these deposits, and discuss their genesis as well as the mechanisms responsible for the geochemical and mineralogical signatures. The deposits chosen for study are unusual because here, contrary to many other metamorphosed Mn deposits, the phases incorporating Sb, As, V, Be, W, the LREE, Ba, and Sr commonly occur as rock-forming minerals. This situation offers an opportunity to recognize textural relationships among the various minerals, and thus, to follow paragenetic evolution through time. Furthermore, small differences in geochemical composition and structural position of the deposits allow study of the influence of these parameters on the redistribution of trace elements during metamorphism.

REGIONAL GEOLOGY

Val Ferrera, a high valley with the source of a tributary to the Rhine in Graubünden (Switzerland), belongs geologically to the Middle Penninic domain (Briançonnais) of the Eastern Swiss Alps, which is characterized by shallow-water sedimentation from Triassic to Middle Jurassic (Trümpy 1980). In Val Ferrera, the Briançonnais platform was segmented into four distinct tectonic units during the Alpine orogeny: (1) the Tambo nappe, (2) the Suretta nappe, (3) the Starlera nappe, and (4) the Schams nappes (Baudin et al. 1995, Schmid et al. 1997; see Fig. 1). The Starlera and Schams nappes are sedimentary units that are disconnected from their basement, whereas the Suretta and Tambo nappes consist of a pre-Alpine basement underlying a thin sedimentary cover. This pre-Alpine basement comprises two main units, the Timun complex and the “Roffnaporphyr”. The latter represents a large volume of Early Permian (268.3 ± 0.6 Ma; Marquer et al. 1998) volcanic to subvolcanic rocks of granitic composition, which underwent a single episode of metamorphism during the Tertiary. The Timun complex, on the other hand, is a polymetamorphic unit that consists of para- and orthogneisses and amphibolites. The Timun complex was subjected to a pre-Alpine eclogite- and amphibolite-facies metamorphism that was overprinted by Tertiary Alpine metamorphism (Nussbaum et al. 1998). The Suretta cover (Fig. 2) consists of locally preserved Permian clastic metasedimentary rocks followed by a basal quartzite (Perno-Triassic), and then by Triassic dolomitic marbles. This series is cut by rift structures filled with mono- and polygenetic breccias containing clasts of dolomite, quartzite, augen gneiss and, in places, hematite–quartz pebbles. All authors agree on a Mesozoic
Fig. 1. Tectonic map of the eastern Central Alps around Val Ferrera, Graubünden, Switzerland. Abbreviations: SB: San Bernardino, SP: Splügenpass. A "?” indicates where the contact between Avers Schistes Lustrés and the Suretta cover is uncertain.
synsedimentary origin of these breccias, although their precise age remains controversial (Liassic to Cretaceous; Baudin et al. 1995, Schmid et al. 1997). The series then grades into marbles and calc-schists, which are not distinguishable from those of the structurally higher tectonic unit, the South Penninic Avers Schistes Lustrés (Figs. 1, 2). The covers of the Suretta and the Starlera nappes are stratigraphically similar, but the Starlera cover is thicker, and the basal quartzite is generally missing.

Décollement and stacking of the Suretta, Starlera and Schams nappes predate the Tertiary metamorphism and thus, all of these units and the related ore deposits underwent a similar Tertiary metamorphic evolution. Four phases of deformation are distinguished (Schreurs 1995, Marquer et al. 1996, Schmid et al. 1997). D1 (Ferrera phase) is a complex event, which started under blueschist-facies conditions estimated at 10 kbar and 400–450°C (Goffé & Oberhänsli 1992, Nussbaum et al. 1998). The main D1 structures, however, developed under greenschist-facies conditions, and consist of large-scale isoclinal folds and a pervasive schistosity (S1) that destroyed most earlier textures and parageneses. The presence of stilpnomelane in the S1 schistosity suggests an upper temperature limit of about 450°C (Nitsch 1970). The age bracket 35–40 Ma is the most realistic estimate of the timing of the temperature peak during D1 (Hurford et al. 1989). The second phase of deformation D2 (Nietemt phase) occurred under greenschist-facies conditions and is, like D1, associated with isoclinal folding; an axial-plane schistosity (S2), however, developed only in the most incompetent rocks. By using the phengite geobarometer of Massonne & Schreyer (1987), Baudin & Marquer (1993) inferred that a decompression of at least 5 kbar took place between D1 and D2. The Bergell granodiorite, dated at 30.13 ± 0.17 Ma (von Blanckenburg 1992), cuts D2 structures, and therefore sets a minimum age for D2 (Liniger 1992). D1 produced a fine crenulation in the most incompetent rocks, and the last event (D4), occurring under brittle
conditions, was responsible for the formation of subvertical N–S-striking faults.

Two kinds of Fe–Mn deposits, both affected by the metamorphism associated with D1, can be distinguished in Val Ferrera: (i) Fe-carbonate veins in the augen gneiss of the Timun complex (Suretta nappe; Grünenfelder 1956), and (ii) carbonate-hosted stratiform Fe–Mn deposits in the Triassic dolomite marbles of the Suretta, Starlera, and Schams nappes (Stucky 1960). The Fe-carbonate veins display a monotonous mineralogical composition consisting of siderite, ankerite, quartz ± stilpnomelane. Locally, “skarns” with aegirine, hematite or magnetite developed at the contact between the Fe-carbonate veins and the augen gneiss. The second type of ore is the focus of this study.

**MINERALOGY OF THE CARBONATE-HOSTED STRATIFORM Fe–Mn DEPOSITS**

The most common ores consist of hematite, quartz, and carbonate (dolomite), with strontian barite and fluorapatite as widespread minor constituents. Depending on the hematite/quartz ratio, the ores have a schistose or massive appearance. Significant amounts of Mn minerals are restricted to the largest deposits (Stucky 1960). All Mn deposits and some of the stratiform Fe deposits contain a range of unusual Sb, As, V, Be, W, Ba, Sr, and REE minerals (listed with their formula in Table 1). In this paper, however, we restrict our description to four deposits, in which the minerals mentioned reveal a paragenetic evolution or appear in special structural settings. The location of these deposits is indicated on Figure 1, and their tectonic and stratigraphic settings are shown in Figure 2. The methods of investigation are described in the Appendix.

**Fianel**

The Fianel deposit is hosted by dolomitic marbles of the Starlera nappe, with no apparent connection to the basal quartzite. Fianel is the largest deposit of hematite exploited in the past in Val Ferrera. The ores show a strong bedding (1 cm to 50 cm), with single beds exhibiting a lenticular shape (Fig. 3a). Fianel also contains Mn ores, which consist principally of silicate–oxide Fe–Mn ores (below referred to as “mixed ores”) containing quartz, rhodonite, spessartine and andradite–calderite garnet, tephroite, rhodochrosite and kutnohorite, aegirine, hematite, braunite, jacobsite, barylite, and strontian barite. The mixed ores are very fine grained, and exhibit complex relationships among the different phases. For example, Figure 4 shows tephroite replacing rhodonite and rhodochrosite as a result of the reaction $\text{Rdn + Rds = Tep + CO}_2(g)$. In the same thin section, replacement of tephroite by calderite has been observed (see Table 2 for compositions of calderite, rhodomite and tephroite).

V–As minerals are very abundant at Fianel. The most spectacular samples consist of mixed ores, which exhibit a red color due to the presence of the vanadatosilicate medaite (Fig. 3b, Table 2). Medaite, $(\text{Mn,Ca})_6(\text{V,As})_5\text{Si}_5\text{O}_{19}(\text{OH})$, was described by Gramaccioli et al. (1982) in the low-grade metamorphosed, radiolarite-hosted Mn deposits of Val Graveglia, Italy. To the best of our knowledge, Fianel is only the second reported occurrence of this mineral. In contrast to the type locality, where medaite is a rare constituent of discordant veinlets, medaite at Fianel represents up to 3 vol.% of the rock and is aligned in the main $S_1$ schistosity (Figs. 3b, d). A further rock-forming V-rich mineral is an unidentified “mixed ore”–Sr phase ($\text{Ca, Fe, Mn, Pb}$) that forms xenomorphic crystals up to 10 µm in diameter. The Mn ores are cut by several generations of veinlets consisting of quartz, rhodonite, rhodochrosite ± aegirine, andradite–calderite garnet, parsettensite, and strontian barite. Where occurring in medaite-rich ores, these veinlets also contain the vanadates palenzonaite, sanerite, and pyrobelonite (cf. Table 1, Fig. 3c). A hydrated Mn vanadate, fianelite, has been discovered in open fractures cutting such veinlets (Brugger & Berlepsch 1996).

In a V-rich mixed ore, we observed one grain of a mineral that is tentatively identified as längebantie on the basis of electron-microprobe data (Table 3); no other method of identification was used in order to preserve this unique grain. Längebantie has been reported from small Längban-type Mn deposits in the Längban and Sjögurvan provinces, Sweden, and at Brandsnuten, Norway (Nysten & Ericsson 1994). The chemical composition of längebantie from Fianel is very similar to that of the Fe-rich längebantie from the Nyberget deposit in Sjögurvan Province (Table 3). At Fianel, the längebantie

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**TABLE 1. CHEMICAL FORMULAE OF THE Sb–As–V–Ba–W–REE–Ba (Sr) MINERALS OBSERVED IN THE VAL FERRERA DEPOSITS**

<table>
<thead>
<tr>
<th>Name</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>Barite (stromian)</td>
<td>(Ba,Sr)SiO$_4$</td>
</tr>
<tr>
<td>Barylite [Br]</td>
<td>BaBe$_3$Si$_2$O$_4$</td>
</tr>
<tr>
<td>Baryglaucite</td>
<td>CaBe$_3$Si$_2$O$_4$(OH)</td>
</tr>
<tr>
<td>Beryl</td>
<td>Be$_6$Al$_2$Si$_2$O$_8$</td>
</tr>
<tr>
<td>Batafite</td>
<td>(Ca$_3$U$_3$)(Ti,Nb,Ta)$_2$(O,OH)$_3$</td>
</tr>
<tr>
<td>Charnockite-(Y)</td>
<td>Y$_2$Si$_2$O$_5$</td>
</tr>
<tr>
<td>Fianelite</td>
<td>Mn$_2$V$_2$Al$_2$O$_7$H$_2$O</td>
</tr>
<tr>
<td>Lăngbanite</td>
<td>(Mn$^{2+}$,Ca,Mn$^{2+}$)Fe$^{3+}$Si$_5$O$_9$(SiO$_2$)$_2$</td>
</tr>
<tr>
<td>Medaite [Med]</td>
<td>(Mn$_3$Ca$_2$Y,AsSi$_5$O$_9$(OH)</td>
</tr>
<tr>
<td>Palenanstonite</td>
<td>Na$_2$Ca$_2$Mg$_2$VO$_4$</td>
</tr>
<tr>
<td>Peramite-(Y)</td>
<td>Y$_2$O$_3$·2CaWO$_4$</td>
</tr>
<tr>
<td>Phenakite</td>
<td>Be$_2$SiO$_4$</td>
</tr>
<tr>
<td>Pyrobelonite</td>
<td>Pb$_2$MnO$_3$(OH)$_2$</td>
</tr>
<tr>
<td>Ramanachale</td>
<td>(Ca$_2$Na$_3$)(Si$_5$T$_3$)O$_6$F$_2$(OH)O</td>
</tr>
<tr>
<td>Sanerite</td>
<td>Na$_2$Mn$_3$Y$_2$Si$<em>6$O$</em>{14}$OH</td>
</tr>
<tr>
<td>Scheelite-powellite</td>
<td>Ca$_2$W$_2$O$_9$ – CaMo$_2$O$_9$</td>
</tr>
<tr>
<td>Tilaite</td>
<td>Ca$_2$Mg$_2$Al$_2$O$_7$F</td>
</tr>
</tbody>
</table>

The symbols are shown in square brackets. Other symbols used in tables and in figures are: As aegirine, An ankerite, Ap fluorapatite, Brn braunite, Cal calcite, Cd t caldelenite, Dol dolomite, Hem hematite, Ktb kutnohorite, Mg magnetite, Ms muscovite, Qtz quartz, Rds rhodochrosite, Rhs rhodonite, Sd siderite, Tep tephroite, and Tlc talc.
Fig. 3. Petrography of sediment-hosted stratiform Fe–Mn ore in Val Ferrera. (a) Outcrop of hematite-quartz ore at Fianel, showing lenticular bedding. (b) Outcrop of medaite-rich (orange vanadatosilicate) mixed Fe–Mn silicate-oxide ore at Fianel. (c) Mn ore (dark, mainly rhodochrosite + rhodonite; light, mainly braunite; cross-cut by veinlets consisting of quartz + rhodochrosite + palenzonaite (Bordeaux red)) at Fianel. (d, e) Microphotographs of the medaite-bearing Fe–Mn mixed ores from Fianel; (d) in transmitted light with parallel polarizers, and (e) under cathodoluminescence. (f) Hematite–kainosilicate–fluorapatite schist from Bergwiesen (JB 31), with two clasts of manganoan calcite (*).
Fig. 4. BSE image of a mixed ore from Fianel, showing a grain of rhodonite undergoing transformation to tephroite.

TABLE 2. CHEMICAL COMPOSITION OF SOME ROCK-FORMING MINERALS IN THE CARBONATE-HOSTED Fe–Mn ORES AT VAL FERRERA

<table>
<thead>
<tr>
<th>Number</th>
<th>Sample</th>
<th>Mineral</th>
<th>#1</th>
<th>#2</th>
<th>#3</th>
<th>#4</th>
<th>#5</th>
<th>#6</th>
<th>#7</th>
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<tr>
<td></td>
<td>JB85</td>
<td>Tep</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>JB85</td>
<td>Rd  n</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td></td>
<td>JB325</td>
<td>Cdt</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td></td>
<td>JB314</td>
<td>Med</td>
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<td></td>
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<td></td>
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<td></td>
</tr>
<tr>
<td></td>
<td>JB131</td>
<td>Sps</td>
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<tr>
<td></td>
<td>JB131</td>
<td>Cal</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td></td>
<td>JB131</td>
<td>Kth</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Average of</td>
<td>10</td>
<td>6</td>
<td>2</td>
<td>11</td>
<td>30</td>
<td>7</td>
<td>6</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

|                |    |        |    |    |    |    |    |    |    |    |
| SiO₂ wt%       | 30.35 (1.49) | 49.41 (0.33) | 34.22 | 37.84 (0.44) | 36.26 (1.13) |    |    |    |    |
| TiO₂           | 0.64 |    |    |    |    |    |    |    |    |
| Al₂O₃          | <0.03 | 4.54 |    |    |    |    |    |    |    |
| V₂O₅           | 0.06 (0.05) | 0.07 (0.04) | 7.32 (0.59) | 0.07 (0.06) |    |    |    |    |
| As₂O₃          | <0.05 | <0.05 | 1.82 (0.51) |    |    |    |    |    |
| Fe₂O₃          | 22.92 |    |    |    |    |    |    |    |    |
| FeO            | 0.13 (0.12) | <0.05 |    |    | 1.79 (0.31) | <0.17 (0.22) | <0.17 (0.22) |    |    |
| CaO            | 0.12 (0.07) | 2.03 (0.33) | 11.32 | 0.45 (0.04) | 4.53 (1.62) | 37.10 (1.39) | 27.86 (1.96) |    |    |
| MgO            | 2.58 (1.58) | 2.70 (0.23) | 0.04 | 0.73 (0.03) | 0.09 (0.04) | 0.85 (0.41) | 1.66 (0.16) |    |    |
| MnO            | 66.65 (1.93) | 47.78 (0.89) | 28.53 | 48.91 (0.27) | 56.19 (1.02) | 17.73 (1.95) | 26.49 (1.65) |    |    |
| SrO            |    |    |    |    | 0.17 (0.13) | 0.03 (0.03) |    |    |    |
| CO₂ (calc.)    |    |    |    |    |    | 41.11 |    |    |    |
| H₂O (calc.)    |    |    |    |    |    | 40.22 |    |    |    |
| Sum            | 99.93 | 102.0 | 101.63 | 99.96 | 99.41 | 96.95 | 96.43 |

Structural formulae:

#1 Si₃₋₅Mnₓ₋₅Mgₓ₋₅O₁₀ (normalization on 3 cations)
#2 Siₓ₋₅Mnₓ₋₅Mgₓ₋₅Caₓ₋₅O₁₀ (normalization on 2 cations)
#3 Siₓ₋₅(Mnₓ₋₅, Feₓ₋₅, Mgₓ₋₅, Caₓ₋₅, O₁₀₋ₓ) = Caₓ₋₅Feₓ₋₅Mgₓ₋₅O₁₀₋ₓ (normalization according to Rickwood 1968)
#4 Siₓ₋₅(Alₓ₋₅, Feₓ₋₅, Mgₓ₋₅, Caₓ₋₅, O₁₀₋ₓ) = Caₓ₋₅Feₓ₋₅Mgₓ₋₅O₁₀₋ₓ (normalization on 12 cations)
#5 Siₓ₋₅(Alₓ₋₅, Feₓ₋₅, Mgₓ₋₅, Caₓ₋₅, O₁₀₋ₓ) = Caₓ₋₅Feₓ₋₅Mgₓ₋₅O₁₀₋ₓ (normalization on 8 cations, Fe⁺ = Feₓ₋₅, Mn²⁺ = Mnₓ₋₅)
#6 (Caₓ₋₅, Mnₓ₋₅, Mgₓ₋₅, Siₓ₋₅)CO₃
#7 (Caₓ₋₅, Mnₓ₋₅, Mgₓ₋₅, Siₓ₋₅)CO₃

The standard deviation (1σ) associated with the electron-microprobe data is shown in parentheses. JB85, JB314, and JB325 are mixed ores from Fianel; JB131 is a fluorapatite – kuthoborite – hematite schist from Bergwiesen.
grain contains a sigmoidal internal fabric that is defined by quartz, and oriented discordantly to the D₁ foliation of the surrounding matrix (Fig. 5). The entire grain is cut by a conjugate set of narrow shears. The inner foliation in lāngbanite likely represents a premetamorphic feature, and the lāngbanite thus probably grew synkinematically with respect to D₁.

Barylite, BaBe₂Si₂O₇, is a common accessory mineral within the S₁ schistosity of the medaite-rich mixed ores (Figs. 3d, e). Beryl occurs at Fianel in two varieties, as anhedral blue grains in discordant quartz veins within hematite – quartz – carbonate ores (type I), and as euhedral crystals in a lens of pink dolomite breccia (type II). Phenakite occurs in some of the pink dolomite clasts. Type-II beryl is associated with As- and REE-rich scheelite–powellite, roméite, bergslagite, and fluorapatite in discordant quartz–dolomite veinlets; during a later stage of metamorphism, these veinlets were infiltrated by a fluid that led to partial replacement of the original grains of fluorapatite by As-rich fluorapatite, and to the appearance of paraniite-(Y) in scheelite–powellite (Brugger et al. 1998).

**Piz La Mazza**

A hematite – quartz – carbonate – fluorapatite – strontian barite schist, up to 1 m thick, crops out at Piz

### Table 3: Composition of Lāngbanite (Electron-Microprobe Data)

<table>
<thead>
<tr>
<th></th>
<th>Fianel #1</th>
<th>Nyberget #2</th>
<th>Fianel #1</th>
<th>Nyberget #2</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂  wt%</td>
<td>9.95</td>
<td>10.15</td>
<td>9.06</td>
<td>9.04</td>
</tr>
<tr>
<td>Sb₂O₃</td>
<td>12.03</td>
<td>13.21</td>
<td>13.39</td>
<td>13.49</td>
</tr>
<tr>
<td>As₂O₃</td>
<td>0.27</td>
<td>0.11</td>
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<td>a.a.</td>
</tr>
<tr>
<td>TiO₂</td>
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<td>1.17</td>
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</tr>
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<td>18.97</td>
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<td>18.97</td>
</tr>
<tr>
<td>MnO</td>
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<td>CuO</td>
<td>0.17</td>
<td>0.04</td>
<td>0.44</td>
<td>0.44</td>
</tr>
<tr>
<td>Sum</td>
<td>99.98</td>
<td>98.14</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### Column 1: lāngbanite (?), mean and standard deviation of nine determinations (electron-microprobe data), sample JB31. Column 2: lāngbanite from Nyberget, Sweden (Nyseten & Ericsson 1994). The Y content reported by Moore et al. (1991) is most likely due to the interference between Y₁ and Y₁⁺ (Nyseten & Ericsson 1994), and thus was omitted. The compositions are normalized to 16 cations, Feₑ[O₄] = Fe²⁺, Σ[O] = 1, and the Mn⁴⁺/Mn²⁺ ratio was calculated to obtain 24 atoms of oxygen per formula unit.

![Fig. 5. BSE image of a lāngbanite (?) grain from Fianel, Val Ferrera. Abbreviations: sz: shear zone, S₁: main schistosity. The matrix contains quartz (dark gray), and a complex assemblage of Fe–Mn silicates, carbonates, and oxides (rhodonite, spessartine and andradite–calderite garnet, tephroite, rhodochrosite and kutnohorite, aegirine, hematite, braunite, jacobsite, and strontian barite).](image-url)
La Mazza (Starlera nappe). As at Fianel, the deposit does not seem to have a direct connection to the basal quartzite. The hematite schist at Piz La Mazza contains spherulitic muscovite that encloses hematite, fluorapatite and, rarely, an yttrium phosphate mineral [xenotime-(Y), or possibly churchite-(Y)], and which is locally finely intergrown with carbonate (Fig. 6a). Fluorapatite is also present in the S₁ schistosity and may further be concentrated along the margin of the spherules (Fig. 6a). Hematite generally defines S₁, but some spherules con-

![BSE images of muscovite spherules from Piz La Mazza, Val Ferrera. Dashed lines delineate the pressure shadows of the spherules. (a) Spherule consisting of muscovite and calcite. Note the yttrium phosphate inclusion [possibly xenotime-(Y)] and the concentration of fluorapatite along the rim; hematite is the predominant mineral in the main schistosity S₁; (b) Muscovite spherule with oriented inclusions of hematite. Note that the orientation of the hematite within the spherule is discordant to S₁.](image)
tain trails of small crystals of hematite oriented discordantly to \( S_1 \) (Fig. 6b). The \( S_1 \) schistosity wraps around the spherules, and a pressure shadow consisting of quartz + hematite is commonly observed (Figs. 6a, b). These features clearly indicate a pre-\( D_1 \) timing for the formation of the spherules.

**Bergwiesen**

The Bergwiesen deposit (Suretta nappe) is a small hematite-rich orebody (up to 2 m thick) that can be followed continuously over 70 m. The concordant nature of the orebody and many examples of fine lamination are well preserved. Although the mineralogy of Bergwiesen contrasts with that of the Starlera deposit (located about 200 m away), both deposits are contained in dolomitic marbles just above the contact with the host garnet (Fig. 8d). The size of the apatite inclusions (\( \leq 5 \mu m \)) in the spessartine grains contrasts with that of the fluorapatite crystals (up to 40 \( \mu m \)) that occur outside the porphyroblasts, aligned in \( S_1 \) (Fig. 8).

Besides Fianel, Bergwiesen is the only deposit where beryl was identified. Here, the mineral occurs, like type-nepheline (Fig. 7).

**Starlera**

The Starlera mine (Suretta nappe) is the only deposit of the province that was exploited for Mn (from 1917 to 1920; Stucky 1960). This deposit is characterized by a complicated paleogeographic and structural position. The ore is hosted in dolomitic marbles, but may be in direct contact with the augen gneiss of the underlying basement (Fig. 7). In the vicinity of Starlera, the basal quartzite exhibits large variations in thickness, from > 20 m at Bergwiesen to zero at Starlera. These variations in thickness might represent a Triassic paleogeography (trough) that favored ore deposition at Starlera. The present thickness of the ore, up to 12 m, also reflects doubling of the sequence by folding. Breccias with a matrix rich in magnesioaugite asbestos are abundant and characteristic of the Starlera deposit.

The Mn ores at Starlera are relatively poor in Si. Braunite is the main ore mineral, and the Mn-silicates rhodonite and spessartine are absent. Fine needles of romanècheite occur along braunite grain-boudaries. The ore is cut by numerous discordant roméite–tilasite veins. The latter are up to 30 mm thick, and display an uncommon mineral assemblage consisting of octahedra of fluorian roméite (\( \leq 5 \, mm \)), coarse-grained tilasite, idiomorphic aegirine, calcite, hydroxyl-phlogopite, and fluorite (Brugger et al. 1997).

Tilasite is also present in some hematite – carbonate – quartz ores that are interbedded between Mn ores and country-rock carbonates. These ores exhibit a banded to lenticular texture. Greenish tilasite is the main constituent of some discordant bands and lenses (up to

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**Fig. 7.** Schematic cross-section illustrating the tectonic setting of the Starlera and Bergwiesen deposits, Val Ferrera.

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**Fig. 8.** Distribution of fluorapatite and spessartine porphyroblasts showing trails of inclusions of hematite in spessartine and that occurring in \( S_1 \).
FIG. 8. BSE images of spessartine in the fluorapatite – kutnohorite – hematite schist from Bergwiesen, Val Ferrera. (a) Spessartine porphyroblast with randomly distributed inclusions of fluorapatite. (b) Spessartine porphyroblast with sigmoidal inclusion-trails of fluorapatite and kutnohorite. (c) Close-up view of fluorapatite inclusions in a spessartine host crystal. (d) Spessartine porphyroblast with a core dominated by fluorapatite inclusions. $S_1$ = main schistosity.
3 cm × 0.5 cm in size). Tilasite also occurs in discordant veinlets (<2 mm in thickness) in this hematite–carbonate–quartz ore.

A complex association of Ti, As, Sb, Be, Ba (±REE, W, Sr) minerals has been described by Brugger & Gieré (1999) from quartz-rich pink muscovite–aegirine–albite schists (hereafter referred to as “pink schists”) interbedded with the Fe–Mn ores. Aligned in the main S1 schistosity are strontian barite, As-poor fluorapatite, ±interbedded with the Fe carbonate veins in the basement rocks are relatively flat, whereas this ratio is low for the Fe ores. Similarly, the Sr contents intermediate between those of the Fe ores and carbonate-hosted rocks, but they all display negative Eu anomalies (Eu/Eu* between <0.1 and 0.7); Ce anomalies range between negative and positive values (Ce/Ce* in the range 0.05–1.99).

**Whole-Rock Composition of the Ores and Their Host Rocks**

The Fe/(Fe + Mn) values of the siderite veins are similar to those of their augen gneiss host-rock (Fig. 9a). In contrast, the carbonate-hosted deposits display a wide range of Fe/(Fe + Mn) values that range between 0 and 1 (Fig. 9b). Whole-rock geochemical data demonstrate that all carbonate-hosted stratiform ores of Val Ferrera are characterized by high concentrations of Sb, As, V, Be, and W relative to both the host rocks and Fe-carbonate veins (Tables 4, 5, Fig. 10).

The W and Be contents of the carbonate-hosted stratiform ores are higher than those of the Fe-carbonate veins and of the country rocks (Fig. 10a). The samples with high Be contents commonly also have high W contents. Two samples with unusual mineralogy do not follow this trend: JB423, which contains >10 vol.% roméite, a phase in which W is highly compatible, and JB101, which contains beryl and scheelite–powellite. In the V versus As diagram (Fig. 10b), there is a marked difference between mixed Fe–Mn ores from Fianel and the Fe ores: at high levels of trace-metal enrichment, the mixed ores generally exhibit a high V:As ratio, whereas this ratio is low for the Fe ores. Similarly, the roméite-rich ore JB423 and one sample of Mn-ore (sample JB161) exhibit a high As:V ratio.

A Sr versus Ba variation diagram (Fig. 11) reveals that Sr contents of the carbonate-hosted Fe and Mn ores are similar to those of the Triassic marbles, but that the Ba contents are much higher in the ores. There is a distinct positive correlation between Sr and Ba in the carbonate-hosted ores, particularly in the mixed Fe–Mn ores from Fianel. The Fe-carbonate veins, on the other hand, are relatively poor in Ba and Sr. Compared to their host rocks, the veins have much lower Sr, but lower Ba contents (~300 ppm in the augen gneiss; Balzer 1989).

Chondrite-normalized REE patterns of the Fe-carbonate veins in the basement rocks are relatively flat, but exhibit a distinct positive Eu anomaly; these patterns are in marked contrast to the pattern of the augen gneiss, characterized by enrichment in LREE relative to heavy REE (HREE) and by a negative Eu anomaly (Fig. 12a). The REE patterns of the carbonate-hosted ores (Fig. 12b) display a greater complexity. (i) Most of the Fe ores have relatively flat REE patterns, exhibiting a wide range of Eu anomalies [Eu/Eu* = 2 EuCN/(SmCN + GdCN)] from <0.1 to 1.32, and a slightly negative Ce anomaly [Ce/Ce* = 2 CeCN/(LaCN + PrCN) = 0.92 to 0.47]. (ii) The Fe-rich ore JB306 has an LREE-enriched pattern, which is relatively parallel to that of the Triassic marbles. The pink ferroan dolomite from the beryl-bearing breccia at Fianel has a similar REE pattern. (iii) Most Mn-rich ores have REE contents intermediate between those of the Fe ores and carbonate-hosted rocks, but they all display negative Eu anomalies (Eu/Eu* between <0.1 and 0.7); Ce anomalies range between negative and positive values (Ce/Ce* in the range 0.05–1.99).

**Discussion**

**Genesis of the Fe-carbonate veins**

The abundance of Fe-carbonates in late (D3?) Alpine vugs within the augen gneiss illustrates the ability of
| SiO₂ | 56.9 | 56.2 | 56.9 | 56.0 | 52.8 | 48.8 | 49.8 | 3.52 | 1.41 | 6.30 | 6.75 | 5.24 |
| TiO₂ | 0.07 | 0.02 | 0.06 | 0.02 | 0.02 | 0.02 | 0.04 | 0.05 | 0.03 | 0.05 | 0.03 | 0.06 |
| Al₂O₃ | 0.29 | 0.04 | 0.21 | 0.11 | 0.10 | 0.13 | 0.08 | 0.07 | 0.12 | 0.25 | 0.17 | 0.37 |
| FeO | 0.37 | 0.11 | 0.35 | 0.22 | 0.35 | 0.32 | 0.35 | 0.40 | 0.10 | 0.58 | 0.20 | 0.64 |
| MnO | 0.54 | 0.31 | 0.12 | 0.35 | 0.32 | 0.25 | 0.17 | 0.12 | 0.12 | 0.15 | 0.40 | 0.40 |
| MgO | 0.26 | 0.52 | 0.84 | 0.30 | 0.60 | 0.30 | 0.75 | 0.26 | 0.77 | 0.56 | 0.76 | 0.76 |
| CaO | 44.50 | 47.16 | 0.09 | 4.37 | 2.73 | 5.79 | 2.28 | 3.60 | 0.19 | 5.10 | 1.85 | 4.77 |
| Na₂O | 0.05 | 0.20 | 0.48 | 0.05 | 0.05 | 0.05 | 0.05 | 0.05 | 0.05 | 0.05 | 0.05 | 0.05 |
| K₂O | 0.15 | 0.07 | 0.06 | 0.16 | 0.05 | 0.05 | 0.05 | 0.05 | 0.05 | 0.05 | 0.05 | 0.05 |
| P₂O₅ | 0.03 | 0.03 | 0.03 | 0.03 | 0.03 | 0.03 | 0.03 | 0.03 | 0.03 | 0.03 | 0.03 | 0.03 |
| Total | 98.11 | 98.81 | 98.81 | 98.81 | 98.81 | 98.81 | 98.81 | 98.81 | 98.81 | 98.81 | 98.81 | 98.81 |
| FeO | 0.29 | 0.29 | 0.29 | 0.29 | 0.29 | 0.29 | 0.29 | 0.29 | 0.29 | 0.29 | 0.29 | 0.29 |
| MgO | 0.26 | 0.26 | 0.26 | 0.26 | 0.26 | 0.26 | 0.26 | 0.26 | 0.26 | 0.26 | 0.26 | 0.26 |
| CaO | 44.50 | 47.16 | 0.09 | 4.37 | 2.73 | 5.79 | 2.28 | 3.60 | 0.19 | 5.10 | 1.85 | 4.77 |
| Na₂O | 0.05 | 0.20 | 0.48 | 0.05 | 0.05 | 0.05 | 0.05 | 0.05 | 0.05 | 0.05 | 0.05 | 0.05 |
| K₂O | 0.15 | 0.07 | 0.06 | 0.16 | 0.05 | 0.05 | 0.05 | 0.05 | 0.05 | 0.05 | 0.05 | 0.05 |
| P₂O₅ | 0.03 | 0.03 | 0.03 | 0.03 | 0.03 | 0.03 | 0.03 | 0.03 | 0.03 | 0.03 | 0.03 | 0.03 |
| Total | 98.11 | 98.81 | 98.81 | 98.81 | 98.81 | 98.81 | 98.81 | 98.81 | 98.81 | 98.81 | 98.81 | 98.81 |

Table 4. Whole-rock compositions of the ores of Val Ferrera.
hydrothermal fluids to mobilize Fe from the augen gneiss. Thus, the augen gneiss is also a likely source for the Fe in the pre-D1 Fe-carbonate veins. Differences between the REE patterns of Fe-carbonate veins and augen gneiss (Fig. 12a) can be explained by derivation of both the Fe and REE in the veins from the augen gneiss. REE are transported as complexes in hydrothermal fluids. The stability of the strong complexes with OH⁻ and F⁻, and therefore the solubility of the REE, increase as the ionic radius of the REE decreases (Haas et al. 1995). However, weaker chloride, carbonate, or hydrocarbonate complexes are more likely to have been present in the fluids involved in the formation of the Fe-carbonate veins. The stability of these complexes changes only slightly with ionic radius of the REE, and therefore the solubility of the REE, increase as the ionic radius of the REE decreases (Haas et al. 1995). However, weaker chloride, carbonate, or hydrocarbonate complexes are more likely to have been present in the fluids involved in the formation of the Fe-carbonate veins. In addition to complexing, crystallographic control may also have been important, perhaps even a dominant, factor in controlling the REE pattern of the Fe-carbonate ores. Siderite is likely to favor incorporation of the HREE owing to the small ionic radius of Fe²⁺ (0.78 Å; Shannon 1976) relative to the radii of the other REE. The positive Eu anomaly in the veins is explained by the preferential alteration of plagioclase in the augen gneiss, as this mineral commonly displays a positive Eu anomaly (e.g., Lipin & McKay 1989).

Aegirine skarns developed locally during metamorphism at the contact between Fe-carbonate veins and augen gneiss host-rock. Where these skarns have a low Na content, they have a REE pattern parallel to that of the siderite ore (Fig. 12a). In this case, the skarn seems to have replaced carbonate ores, and the REE were essentially immobile. At higher levels of Na, however, the skarns display a strong HREE depletion (Fig. 12a). Normal Fe-carbonate ores have low Na contents (<0.05 wt% Na₂O), and therefore, the Na in the skarn had to be carried by the fluid responsible for skarn formation. The correlation between high Na content and HREE depletion in the aegirine skarns indicates that the metasomatic fluid responsible for Na enrichment has also preferentially removed HREE from the Fe-carbonate ore. Fluid flow in D₁ shear zones within the Roffna porphyry induced breakdown of albite, releasing Na into the fluid.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Deposit</th>
<th>Rock type</th>
<th>Mineralogy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Triassic marble</td>
<td>near Fianel</td>
<td>Pink marble (stained by Hem)</td>
<td>Cal, Dol ± Tic, Ms, Hem</td>
</tr>
<tr>
<td></td>
<td>near Fianel</td>
<td>White marble</td>
<td>Cal = Qtz, Ms</td>
</tr>
<tr>
<td>Fe-carbonate veins in augen gneiss</td>
<td>Samanada Sura</td>
<td>Ae-Mgt skarn</td>
<td>Qtz, Mgt, Ae, Ms ± amphibole (winchite)</td>
</tr>
<tr>
<td>JH140</td>
<td>Marteign</td>
<td>Ae-Hem skarn</td>
<td>Qtz, Hem, ± Ae, Ms</td>
</tr>
<tr>
<td>JH122</td>
<td>Samanada Sura</td>
<td>Ank-rich Fe-carbonate ore</td>
<td>Qtz, Ank, Ms</td>
</tr>
<tr>
<td>JH124</td>
<td>Samanada Sura</td>
<td>Sd-rich Fe-carbonate ore</td>
<td>Sd, Ank, ± Qtz, Ms</td>
</tr>
<tr>
<td>JH156</td>
<td>Marteign</td>
<td>Fine grained Fe-carbonated ore</td>
<td>Qtz, Ms, Ank, Sd</td>
</tr>
<tr>
<td>Carbonate-hosted deposits</td>
<td>Bergwiesen</td>
<td>Apatite schist</td>
<td>Ap, Kth, Qtz, Ms, ± Tic, Cal</td>
</tr>
<tr>
<td>JH133</td>
<td>Bergwiesen</td>
<td>Finely laminated Hem-Qtz ore</td>
<td>Qtz, Hem, ± Ms</td>
</tr>
<tr>
<td>JH100</td>
<td>Fianel</td>
<td>Hem-Qtn ore</td>
<td>Qtz, Hem, ± Ms</td>
</tr>
<tr>
<td>JH101</td>
<td>Fianel</td>
<td>Hem-Qtn-carbonate ore</td>
<td>Qtz, Hem, Dol, Tic, ± Ms</td>
</tr>
<tr>
<td>JH105</td>
<td>Fianel</td>
<td>with pink carbonate clasts</td>
<td>Qtz, Hem, ± Ms, Tic</td>
</tr>
<tr>
<td>JH147</td>
<td>Fianel</td>
<td>Med-rich mixed ore</td>
<td>Qtz, Hem, ± Med, Ms, Ae, Kth, Rds, Btt</td>
</tr>
<tr>
<td>JH166</td>
<td>Fianel</td>
<td>Mixed ore</td>
<td>Qtz, Hem, ± Kth, Ae, Ms, Tic, Ap</td>
</tr>
<tr>
<td>JH302</td>
<td>Fianel</td>
<td>Pyroserite</td>
<td>Ae, Qtz, Dol, Cal, Btt, Ap</td>
</tr>
<tr>
<td>JH320</td>
<td>Fianel</td>
<td>Pink Dol clast from the Be-Mo-W breccia</td>
<td></td>
</tr>
<tr>
<td>JH306</td>
<td>Starlera</td>
<td>Hem-Qtn-carbonate ore</td>
<td>Hem, Qtz, Brn, pyrolusite(?), Cal</td>
</tr>
<tr>
<td>JH92</td>
<td>Piz La Mazza</td>
<td>Schistose Hem-Qtn-carbonate ore</td>
<td>Qtz, Hem, Kth ± Ms, Tic</td>
</tr>
<tr>
<td>JH337.1</td>
<td>Schmoorratsrat</td>
<td>Johnnitesite-bearing oxide ore</td>
<td>Hem, jacobsite, Kth ± amphibole (winchite), Dol, Kth</td>
</tr>
<tr>
<td>JH407</td>
<td>Schmoorratsrat</td>
<td>Jacobsite ore</td>
<td>jacobsite, Hem, amphibole, Ms</td>
</tr>
<tr>
<td>JH423</td>
<td>Val Steria</td>
<td>Roméite-bearing ore</td>
<td>Ank, Ap, Qtz, ± Hem, Cal, Ms, Btt</td>
</tr>
</tbody>
</table>

The minerals listed are those identified by X-ray powder diffraction.
Furthermore, overgrowths of Y- and HREE-rich minerals around grains of zircon in the shear zones document the ability of this fluid to mobilize HREE (Vocke et al. 1987). A similar metamorphic fluid probably interacted with the Fe-carbonate veins to form the skarn.

Age of the carbonate-hosted stratiform Fe–Mn mineralization

Occurrence of hematite–quartz pebbles in synsedimentary Mesozoic (Liasic–Cretaceous?) breccias implies synsedimentary to diagenetic formation of the stratiform ores hosted by the Triassic carbonates. The concordant nature of the orebodies and their internal structures, particularly the finely laminated alternations of ore and carbonate, suggest a syngenetic origin of the mineralization. This conclusion, which is based on field relations, is supported by some of the microtextural observations presented here. The carbonate–muscovite schist at Piz La Mazza might represent relict sedimentary structures, e.g., pellets or clay aggregates; the latter may have been important in scavenging certain elements. In particular, sorption on clays could explain the enrichment of the spheres in Y and P [e.g., Aja (1998) for REE]. At Bergwiesen, the tiny crystals of arsenian fluorapatite preserved within spessartine porphyroblasts are consistent with the fine-grained nature of syngenetic ores (e.g., Binns et al. 1993, Hein et al. 1994).

The growth of minerals such as lagenbanite, medaite, arsenian fluorapatite, and barylite in the main S1 schistosity of the Fianel ores indicates that the elements Sb, V, As, Be, and Ba were present in the rocks during D1. No syn-D1 mineral of tungsten was observed, but the trend linking W and Be (Fig. 10a) suggests a genetic link between these elements. Vanadium and As are characteristic of many syngenetic Mn deposits, and the presence of high As contents has been considered diagnostic of the exhalative origin of syngenetic deposits (Marchig et al. 1982). A positive correlation between the levels of As and Sb has been observed in some recent metaliferous sediments of volcanogenic hydrothermal origin (e.g., Karpov & Naboko 1990, Pearcy & Petersen 1990).

In our samples, the correlation is poor, but in general, the As contents are higher where the Sb contents are elevated. Mobility of Be and W in epithermal systems is documented by the large deposits of bertrandite in Utah (Staatz & Carr 1964), and by some active continental hydrothermal systems such as Waiotapu, New Zealand (Hedenquist 1983) and Uncia, Bolivia (White 1974). Thus it seems likely that the carbonate-hosted stratiform Fe–Mn deposits in Val Ferrera became enriched in Sb, As, V, Be, and W during ore formation. Alternatively, some or all of these elements may have been transported into the orebodies at a later stage, e.g., by epithermal or metamorphic fluids that reacted with the Fe–Mn ores. However, there is no evidence to support such a two-stage history. In the study area, no post-Triassic magmatic activity is documented that could have produced such fluids. In particular, the intrusion of the Bergell granodiorite clearly postdates D2 and thus also enrichment of the ores in Sb, As, V, Be, Ba, Sr, and W. Moreover, all of the investigated carbonate-hosted deposits display similar geochemical features, such that
any postulated post-ore event must have acted on a
regional scale. In Val Ferrera, however, mineralization
indicative of the presence of such fluids occurs exclu-
sively in the carbonate-hosted stratiform Fe–Mn ores.
In particular, no evidence is found in rocks such as the
pre-D1 Fe-carbonate veins (Figs. 10a, b) or the calc-
schists of the Suretta and Starlera nappes (Fig. 2), which
likely would have reacted with such a regional fluid.
On this basis, we conclude that enrichment of the ores
in these trace elements occurred simultaneously with ore
formation.

Transport and deposition of metals into
the carbonate-hosted stratiform deposits

The wide range of Fe/(Fe + Mn) values found in the
carbonate-hosted deposits contrasts with the restricted
range observed for the Fe-carbonate veins (Fig. 9).
Krauskopf (1957) showed that a separation between Fe
and Mn can arise from the different relative stabilities
of Fe and Mn oxyhydroxy-minerals as a function of Eh
and pH. For example, a progressive oxidation of a re-
ducing fluid generates first the precipitation of Fe, and
later the precipitation of Mn. The strong redox gradient
located near the sediment–seawater interface is a favor-
able location for such a process, as is demonstrated by
modern-day black smokers (Bonatti 1975).

Metals in syngenetic Fe–Mn deposits can be derived
either from seawater (hydrogenetic) or from sub-sea-
floor sources (exhalative). In the latter case, Huebner et
al. (1992) distinguished between hot hydrothermal flu-
ids and cold diagenetic fluids. Many variation diagrams
have been developed to discriminate between a
hydrogenetic and an exhalative origin of the metals in
syngenetic Fe–Mn ores. In our opinion, however, most
of these diagrams are of little value for carbonate-hosted
deposits. In particular, the classic triangular Mn–Fe–(Co
+ Ni + Cu) diagram of Bonatti et al. (1972) was devel-
oped for deep-sea deposits, where rates of sedimenta-
ton are low. The Val Ferrera ores plot in the hydrother-
mal field of this diagram (low content of transition
metals), but so do Swiss oolitic and residual ores
(Serneels 1993, and unpublished data by Serneels),
which are unlikely to have a significant (if any) hydro-
thermal component. Similarly, the Val Ferrera ores plot
in a restricted area within the hydrothermal fields in the
diagrams Si versus Al (Crerar et al. 1982), Fe:Ti versus
Al, and Mn:Ti versus Al (Barrett 1981). These latter
diagrams, again, were developed for deep-sea environ-
ments, and reflect the competition between rapid depo-
sition of Si, Fe, and Mn from hydrothermal fluids and
slow input (below the calcite-compensation depth) of
detrital Ti and Al. These diagrams, therefore, are not
suitable for deposits forming on a carbonate platform,
where sedimentation is much faster and dominated by
biogenic carbonates.

On the other hand, the presence of significant quan-
tities of As, Sb, W, and Be strongly suggests a hydro-

---

**Fig. 11.** Sr versus Ba variation diagram showing the compositional trends of the various types of ore. Data from Table 4 and from Brugger (1996).
The Sr versus Ba diagram (Fig. 11) suggests different sources for Sr and Ba. The Sr contents of the ores are similar to those of the enclosing carbonates; Ba contents, however, are generally much higher in the ores. Barite is the main carrier of Ba and Sr in the ores and, according to Putnis et al. (1992), its Ba/Sr depends on the Ba/Sr value in the fluid. The positive correlation between Sr and Ba in the ores (Fig. 11) could thus be explained by precipitation of barite, a process that most likely takes

![Diagram](image)

**Fig. 12.** Chondrite-normalized REE patterns of (a) ores from the siderite veins, compared to the augen gneiss analyses of Vocke et al. (1987), and (b) Mn and Fe ores from Val Ferrera, compared to those of the carbonate host-rocks. Chondrite data from Evensen et al. (1978).
place where Ba-rich, sulfate-free hydrothermal waters mix with Sr- and sulfate-rich seawater.

The REE patterns of the carbonate-hosted ores plot between those of two end members, one defined by Fe ores (La/CN/LuCN ≈ 1), and the other by the Triassic marble host-rocks (La/CN/LuCN >> 1); data for the Mn ores typically plot in between (Fig. 12b). At first glance, this position seems to indicate mixing between a hydrothermal fluid and seawater (cf. Fig. 13a for modern analogue), and such simple relationships have been invoked, for example, to explain systematic variations in the REE patterns of banded-iron formations (Kato et al. 1998). One anomalous, Fe-rich sample (JB306), however, plots close to the enclosing marbles, and its REE pattern is very similar to that of a dolomite clast from the pink dolomite breccia at Fianel (Fig. 12b). Some modern hydrothermal sediments have REE patterns and contents that are similar to those of the carbonate-hosted ores from Val Ferrera (Fig. 13b). In particular, the Fe ores from Val Ferrera exhibit a strong similarity to nontronite-rich Fe oxyhydroxide sediments in seafloor chimneys and mounds, which are characterized by concave REE patterns, slightly negative or no Ce anomalies, and negative Eu anomalies (Hekinian et al. 1993; Fig. 13b). The anomalous Fe-rich sample (JB306) has a REE pattern similar to those reported for Fe-sulfide mud and silica-rich Fe oxyhydroxides from the East Pacific rise (Fig. 13b). These modern samples probably do not contain a significant hydrogenic component (Hekinian et al. 1993), reflecting the importance of mineralogical controls on the REE patterns of the sediment. Therefore, it appears difficult to interpret quantitatively the REE patterns of metamorphosed deposits, where the original mineralogy of the sample and its location relative to submarine vents are obscured. This problem is exacerbated, in our case, by the fact that the depositional environment of the Val Ferrera ore (shallow carbonate platform) was very different from that of the deep oceanic deposits. Nevertheless, similarity of the REE patterns of the Val Ferrera ores with those of modern proximal hydrothermal sediments strongly suggests that they share a similar exhalative origin.

Variability of the Eu and Ce anomalies furnishes a strong argument for ore formation at a pronounced redox boundary, such as that existing at the interface between sediment and seawater. The strongly oxidizing conditions required for the stability of Ce⁴⁺ are rarely obtained in the Earth’s crust. Oxidation of Ce³⁺ to Ce⁴⁺ does occur in seawater, even if the precise mechanisms involved remain unclear. Equilibrium thermodynamics (Liu et al. 1988), surface reactions on Mn oxyhydroxides (Brookins 1989 and references therein), and bacterial activity (Moffett 1990) all have been invoked. Repeated precipitation (at the contact with seawater) and redissolution (as burial brings the newly formed chemical sediment to reducing conditions) may produce the random Eu and Ce anomalies observed in the carbonate-hosted ores.

No trace of volcanic or magmatic activity could be observed in the marbles in proximity to the studied deposits. Concordant layers of amphibolite, however, occur in the dolomitic marbles of the southern part of the Suretta nappe and probably represent meta-tuffs (Gieré 1985). Similarly, the thick Triassic series (about...
600 m) of the Tscher–Kalkberg 2b unit (Rück 1995) in the Schams Nappes contains many tuffaceous layers; these are particularly abundant in the Upper Anisian (where a pumice layer is present) and Lower Ladinian, but occur also in the Lower and Middle Anisian as well as in the youngest Upper Ladinian (Streiff et al. 1976). Moreover, synsedimentary tectonic movements are documented in the Triassic of the Schams nappes, for example, by different transgressive horizons and by the occurrence of monogenic and polygenic breccias (Streiff et al. 1976). Therefore, we conclude that the thermal conditions and tectonic setting for the activation of distal epithermal systems within the Suretta basement were present during the Triassic.

On the basis of the arguments presented above, the carbonate-hosted deposits most likely represent Triassic synsedimentary exhalative deposits, and the As, Sb, V, Be, W, Ba, Sr, and the REE were introduced simultaneously with the Fe and Mn oxyhydroxide minerals. Most elements were supplied by a hydrothermal fluid that circulated in the basement. Exceptions are S and possibly Sr, which are considered to be derived mainly from seawater.

**Premetamorphic mineralogy of the carbonate-hosted ores**

By analogy with modern seafloor syngentic exhalative deposits, such as on Franklin Seamount in the Western Woodlark Basin (Binns et al. 1993), the original mineral assemblage of the Val Ferrera deposits may have comprised carbonates, Fe–Mn hydroxides and oxides, silica, and strontian barite. The elevated Na content of some Fe–Mn ores in Val Ferrera could be related to primary minerals such as vernadite [Fe5+O4(OH)2·9H2O], birnessite [Na4Mn14O27·9H2O], and nontronite [Na8·7(Fe3+6.3)/6(Si,Al)O3(OH)·nH2O], which are major constituents of some Fe–Mn crusts of hydrogenetic and hydrothermal origin (Bolton et al. 1988, Binns et al. 1993). Sodium enrichment also is known from other places in the Suretta cover: farther known from other places in the Suretta and Starlera nappes, no phosphorites are reported from modern deposits, but abundant tilasite-rich precursor phase. Such phases have not yet been reported from sedimentary ores, but abundant tilasite occurs in other metamorphosed Mn deposits. Dolomite–tilasite marble occurs in polymetamorphic Precambrian rocks at Nežilovo, Macedonia (T < 500°C, P > 2 kbar; V. Bermanec, written commun.); it is associated with a regional enrichment in Ba, Zn, Pb, Cu, Mn, Ti, REE and As attributed to syngentic exhalative processes (Bermanec et al. 1993, Bermanec 1994). Tilasite–rich veins have also been described from the sediment-hosted, zeolite-facies-metamorphosed Mn ores at Djebel Guettara, Algeria (Heflik 1989). Tilasite thus occurs under very broad P–T conditions, and might even be a syngeneric to diagenetic phase in some deposits. Colloidal Mn oxyhydroxides from recent hydrothermal deposits contain up to 0.18 wt% W (Kirchheimer 1959), and Be can be hosted in rhodochrosite in considerable quantities (up to 0.3 wt% BeO, Grigor’yev 1967).
Genetic link between Fe-carbonate veins and sediment-hosted stratiform deposits?

The available lines of evidence do not allow us to reject a direct genetic link between the Fe-carbonate veins in the basement and the carbonate-hosted deposits; the former possibly acted as feeder channels for the latter. Both formed prior to the D1 event, but no further clue to their relative age is available. The augen gneiss is a likely source for the Mn and Fe (and possibly other elements) found in both types of deposits. The pronounced difference in trace-element profile of these deposits can be explained in terms of the markedly different conditions of ore formation: (1) The Fe-carbonate veins were deposited within pre-Triassic orthogneisses of the basement; they acquired a simple assemblage (Fe-carbonate), where the minerals were probably well crystallized and relatively coarse-grained. In contrast, the carbonate-hosted deposits formed at or close to the sediment–seawater interface, comprising a complex association of poorly crystalline Fe–Mn oxyhydroxides. Adsorption most likely did not play a significant role during formation of the Fe-carbonate veins (higher temperature, unfavorable mineralogy, low surface-area), but it was a fundamental process during formation of the carbonate-hosted deposits, where elements like As, Sb, V, and possibly Be, W, and REE were scavenged. (2) In contrast to the Fe-carbonate veins, deposition of the carbonate-hosted ores took place in an environment with a pronounced redox gradient. This redox gradient was responsible for the separation of Fe and Mn, for variability of the Eu and Ce anomalies, and it may have controlled the deposition of other redox-sensitive trace elements (e.g., As, V, Sb). (3) The presence of sulfate in seawater was most probably responsible for the precipitation of Ba and Sr as strontian barite; elements like Sr and S were likely partially derived from seawater.

Paragenetic evolution during metamorphism

Tertiary metamorphism induced recrystallization and breakdown of the primary Fe and Mn minerals. The behavior of Sb, As, V, and Be during D1 was controlled by the mineralogical and geochemical composition of the protolith. In Fe-rich deposits, hematite can accommodate relatively high contents of As and V (e.g., Piz La Mazza; Fig. 14). Indeed, a complete solid-solution exists between FeO and V2O3 (Cox et al. 1962). Thus, As and V were still highly compatible with regard to the metamorphic mineral (hematite), compared to the syngenetic phase (poorly crystalline Fe oxyhydroxide), inhibiting the formation of metamorphic arsenates and vanadates. Fluorapatite and its precursor phase played a similar role for As in the fluorapatite – kutnohorite – hematite schists of Bergwiesen (Fig. 15a). Arsenic is strongly compatible in fluorapatite, and metamorphic recrystallization did not release much arsenic. In contrast, Sb, As, V, and Be tend to accumulate in synkinematic accessory minerals in mixed ores at Fianel (Fig. 15b). Here, medaite, lándganite, barylite, and arsenian fluorapatite grew during D1 metamorphism.

At Starlera, the only syn-D1 As-bearing minerals found are fluorapatite with low As contents in the pink schists (Fig. 15d), and tilasite in some hematite – carbonatite – quartz ores (Fig. 15e). No unambiguous syn-D1 phase rich in Sb has been identified so far at Starlera; this contrasts with the large amounts of Sb contained in the discordant tilasite–roméite veins characteristic of this locality (Brugger et al. 1997). The pink schists at Starlera contain a complex mineral assemblage that evolved mainly after D1, characterized by Sb, As, Be and REE minerals (Fig. 15d). Moreover, the Ti minerals titanite, pyrophanite, and some rutile grew after D1 and incorporated considerable amounts of Sb and As, thus recording elevated contents of these metals in a post-D1 fluid. Post-D1 remobilization of certain elements (i.e., V, As, Be) is further documented by the mineralogy of discordant veinlets and open fractures in the mixed ores at Fianel (Fig. 15b). Also at Fianel, a lens of dolomitic breccia contains Sb, As, Be, Mo, and W minerals in discordant veinlets and in pressure shadows of dolomitic clasts (Fig. 15c); a metasomatic event subsequently led to the formation of paranelite-(Y) within the scheelite–powellite, and of As-rich fluorapatite along the rim of fluorapatite grains (Fig. 15c; cf. Brugger et al. 1998). The latest stage of the metamorphic evolution produced narrow open fractures in the Fianel deposit: in the mixed ores, the fractures contain fianelite (Brugger & Berlepsch 1996), which formed as a product of weathering of nearby palenzoomite (Fig. 15b), whereas in the dolomite breccia the open fractures host powellite crusts, scheelite–powellite, chernovite-(Y), and barite (Fig. 15c; Brugger et al. 1998).

The post-D1 history of the mobilization of the trace elements is indeed complex. A major problem results from the difficulty of correlating the paragenetic successions found in different types of ore with each other, and with the regional tectonometamorphic evolution. The complex mineralogy of the Fe–Mn ores contrasts strongly with that of the country rocks; the latter consist of granitic gneisses and marbles that were mineralogically relatively inert following D1. The complex discordant veins that are common in the Mn ores have no equivalent in the host rocks. The abundance of post-D1 magnesiorebeckite in the breccia at Starlera also is a unique feature, which might be related to hydrothermal fracturing during D2 deformation; thick roméite–tilasite veins of the Starlera deposit could also be attributed to this event (Fig. 15e). The unusual mineralogy of the pink schists is due to their characteristically high Ti content, which is probably mainly the result of a high proportion of detrital components in the protolith (cf. rounded grains of rutile). This high primary Ti content also renders the pink schists a likely source for the Ti in roméite of the late roméite–tilasite veins. In addition, the pink schists represent preferential flowpaths for fluids that
eventually produced the roméite–tilasite veins, and the post-D$_1$ growth of Sb-rich titanite and stiboan rutile; growth of associated minerals in the matrix of the pink schists (Fig. 15d, “post-kinematic”) may be related to this fluid.

**Comparison with other metamorphosed Fe–Mn deposits**

The carbonate-hosted stratiform Fe–Mn deposits of Val Ferrera share many mineralogical and geochemical features with the Carboniferous Mn deposits in the central Pyrénées. Detailed textural and structural investigations led Ragu (1990) to infer a syngenetic exhalative origin for these deposits, which were subsequently subjected to a Hercynian upper-greenschist-facies regional metamorphism. Intrusion of large volumes of late Hercynian granites produced a second metamorphism under greenschist-facies conditions. The deposits of the Pyrénées are characterized by high V and Ba concentrations (no whole-rock data exist for Sb, As, Be, and W), and in some of these deposits As, V, Be, and W...
**Fig. 15.** Synopsis of the paragenetic evolution in some Fe–Mn deposits and ore types from Val Ferrera. (a) Bergwiesen, fluorapatite – kutnohorite – hematite schist; (b) Fianel, “mixed ores”; (c) Fianel, pink dolomite breccia; (d) Starlera, pink schists; (e) Starlera, other lithologies. The correlations among the post-D1 parageneses in the different deposits and rock types are not well constrained: the discordant veins in (a) and (b) are most likely synchronous, but the temporal relationship between these veins and the post-S₁ features shown in (c) and (d) are unknown. At Fianel, the open fractures in the mixed ores (b) are probably younger than those in the pink dolomite breccia (c). The horizontal shading emphasizes minerals that are stable over different stages (light gray), as well as the evolution of the carriers of trace elements like Be and V at Fianel (darker shade).
minerals occur in discordant veinlets (Ragu 1990, 1994, Brugger et al. 1999). Ragu (1994) argued that the elemental association found in these veins implies an input of at least Be and W from hydrothermal fluids originating in late Hercynian granites. The example of Val Ferrera suggests, however, that the Sb + As + V + Be + W association may also develop in a syngenetic environment. Thus, the occurrence of this association of elements in metamorphic veins should not be used as the sole geochemical indicator for a magmatic origin of the metamorphic fluids.

The mineralogy of the Val Ferrera ores is similar to that of radiolarite-hosted deposits in the Central Alps (e.g., Falotta, Praborna) and in the Ligurian Alps. The mineralogical resemblance points to similarities in metamorphic evolution, but also in the geochemical composition of the protolith. Noteworthy is the fact that the two types of deposits formed under very different conditions, i.e., near a mid-oceanic ridge over basaltic rocks (radiolarite-hosted deposits), and on a carbonate platform above a granitic basement (Val Ferrera deposits). Therefore, the hydrothermal fluids must have acquired their metal contents through interaction with markedly different types of rock. Similarity of the ore composition is probably a consequence of the similar conditions that existed during ore deposition (mixing of hydrothermal fluid with seawater) and of the processes responsible for enrichment of the trace elements considered (control by ore mineralogy). The particularly high Be and W contents of the Val Ferrera ores, on the other hand, can be related to occurrence of the deposits above a basement characterized by abundant rhyolites and granites. Remobilization of Be and W, together with As and REE, from Early Permian rhyolites has recently been documented also in other parts of the Alps (Knill 1996). Moreover, the Mn mineralization at Guettara, Algeria, is associated with Precambrian rhyolites and is particularly rich in As and Be (Agard 1965). Similarly, the Mn deposits at Lángban (Boström et al. 1979) and Franklin (Dunn 1995) occur in carbonates deposited on continental crust and are well known for their Be and W minerals.

Comparison with element mobility in other geological settings

The joint mobility of high-field-strength elements (HFSE), large-ion lithophile elements (LILE), and LREE has been reported under very different P–T conditions and geodynamic settings, such as in subduction zones (e.g., Sorensen & Grossman 1989, Philippot & Selverstone 1991) and within the mantle (e.g., Harte 1987). These examples are of particular interest because there metasomatism affects the global geochemical cycles of various elements. In both cases, metasomatism is closely associated with magmatism. Volatiles reduce the solidus temperature, and, by altering the composition of the source region of magmas, metasomatism also influences the chemistry of the magmas (Lehmann et al. 1994).

A common feature of the element mobility in Val Ferrera, in subduction zones and in mantle metasomatism, is the importance of the stability of Ti minerals in controlling element mobility: titanite, rutile, and roméite in Val Ferrera; titanite and rutile in subduction zones (Philippot & Selverstone 1991), and titanian magnetite, titanite, crichtonite, armalcolite, and hollandite-type structures in mantle metasomatism (Harte 1987, Ionov et al. 1999). The structural properties of some of these minerals ensure that they are a major sink for both HFSE (in the Ti site), LILE, and LREE (in interstitial sites).

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References


Petrographic studies have been carried out on standard polished sections 30 μm thick. Because of the generally small grain-size and complex mineral associations in the ores, we used a methodological approach that included transmission and reflection optical microscopy, cathodoluminescence (Technosyn Cold Cathode Luminescence Model MKII, operated at 25 kV and 100 μA), and electron microscopy in both secondary electron (SE) and back-scattered electron (BSE) modes. Cathodoluminescence (CL) has proven to be a very powerful method for easily finding strontian barite (yellow), fluorapatite (yellow to green), barylite (blue), bergslagite (pale blue), and an yttrium phosphate (bright blue). CL further revealed zoning in fluorapatite, barite, and carbonates.

Quantitative chemical analyses of minerals were carried out with a JEOL JXA–8600 electron microprobe at the Institute for Mineralogy and Petrography, University of Basel, Switzerland, with analytical conditions and standards similar to those used by Brugger & Gieré (1999). Geochemical analyses of major and some trace elements were made of 59 whole-rock samples by X-ray fluorescence (XRF) at the University of Lausanne, Switzerland, following the procedure of Pfeifer et al. (1991). Inorganic CO₂ was determined by coulometric titration, using N₂ as a carrier gas. Analyses of five different whole-rock samples were repeated using O₂-rich gas to oxidize the “organic” carbon (present as graphite) in the sample, and yielded the same CO₂ content within analytical error. Concentrations of an extended set of trace elements were measured by inductively coupled plasma – mass spectrometry (ICP–MS) at Service d’Analyse des Roches du CNRS, Nancy, France on 20 samples previously analyzed by XRF.