

Isotope geochemistry (S, C, O, Sr, Pb) of the Chaudfontaine mineralization (Belgium)

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Abstract. Investigations on S, C, O, Sr, and Pb isotopes in ores, gangue, and country rocks of the Chaudfontaine ore deposit confirm that interbedded barite and white sparry calcites are cogenetic. They emphasize the marine origin of S and the nonmarine origin of the metals. They underline the important role played by the bacterial reduction at the site of deposition. Hypotheses concerning the source of the metals and the nature of the brines involved in their transportation are briefly discussed.

Isotope geochemistry is a powerful tool in deciphering the petrogenesis of rocks in general and of ore deposits in particular. However, some metallogenists are not wholly convinced of the merits of this technique. Indeed, in some cases, results based on a small amount of data have led to premature conclusions. In other cases, conclusions have been drawn without taking into account all the geological constraints. Sometimes, detailed isotope studies on several different elements have resulted in contradictory conclusions (Routhier 1980, p. 170–171). Isotope geochemistry should thus be used with caution and the isotope results should be considered in conjunction with all other available data.

These few unfortunate examples should not, however, make us forget the numerous cases for which the contribution of isotope geochemistry has been essential. The synthetic works of Fritz (1976) on C and O isotopes, Sangster (1976) on S and Pb isotopes, and Köppel & Saager (1976) on U, Pb and Th isotopes constitute fruitful contributions.

This study demonstrates the usefulness of the integration of several isotope systems, both stable (S, C, O) and radiogenic (Sr, Pb), in understanding the genesis of a sedimentary barite ore deposit, i.e., that of Chaudfontaine (Belgium).

The Chaudfontaine ore deposit and its geological environment

The Chaudfontaine ore deposit (Dejonghe 1979, 1985) is situated within the Verviers synclinorium (Graulich et al. 1984; Graulich & Dejonghe 1986) which is subdivided into three tectonic subunits, i.e., the Herve massif, the Vesdre massif, and the Theux tectonic window.

A detailed geological map of the Chaudfontaine area is presented in Fig. 1. The bedrock is exclusively made up of sedimentary rocks of various ages (from Lower Devonian up to Silesian) and of various lithologies (alternating

sandstones, shales, and carbonates, see Fig. 1). This region is tectonically complex: It is cut by numerous overthrust faults, and an overthrust sheet (Chèvremont) is pinched between the Vesdre and Herve massifs. Two NS geological cross sections (Fig. 2) illustrate the tectonic pattern of the area, which consists of a succession of wide synclines and narrow anticlines with frequently fractured or even faulted axial planes. A comparison of these two parallel sections, 375 m apart, gives an appreciation of the tectonic variations of this area. The position of the mineralized level of Chaudfontaine is plotted on each of the cross sections.

The ore deposit is characterized by the alternation of strongly mineralized layers, barren beds, and various combinations of these two extremes. The ore is chiefly made up of barite with accessory pyrite, sphalerite, and galena. Under the microscope, scarce small inclusions of chalcopyrite and bravoite have also been identified (Dejonghe 1978; Dejonghe et al. 1985). The main forms of the barite crystals as well as the sedimentary structures in which they occur have been described by Dejonghe (1979, 1985).

The orebody has been intersected by three drill holes (enumerated by the Geological Survey of Belgium as 134 E 303, 134 E 310, and 134 E 396, Fig. 1). The drill sites occupy the vertices of a right-angle triangle, the right-angle sides of which measure 180 and 375 m in length. The orebody is located on the two flanks of a faulted anticline shown in Fig. 2 at vertical depths between 180 and 210 m. In the three drill holes the mineralization is situated at the same stratigraphic level, i.e., at the top of the Frasnian. More precisely, using the terminology of Coen-Aubert & Lacroix (1979), it is located at the top and above the second *Phillipsaetraea* biostrome of the Aisemont Formation.

The fluid inclusions of the barite have been studied by Dejonghe et al. (1982 b) and Dejonghe (1985). All the syngenetic inclusions are single phase at room temperature. The lack of a gas bubble requires a very low filling temperature, certainly below or equal to 50°C (Sabouraud et al. 1980). The mean salinity deduced from the histogram is 16.5 equiv. wt% NaCl. At their highest concentrations, the brines have reached salinities of up to 23 equiv. wt% NaCl. If the salinities of the Frasnian seas were identical to those of the present-day seas, it would correspond to a mean concentration by evaporation of about one-fifth of the original volume (Sabouraud-Rosset 1976, p. 72).

In drill hole 134 E 396, at two levels (between 195.50 m and 196.45 m and between 202.70 m and 202.90 m), barite is accompanied by very white sparry calcite, which is locally

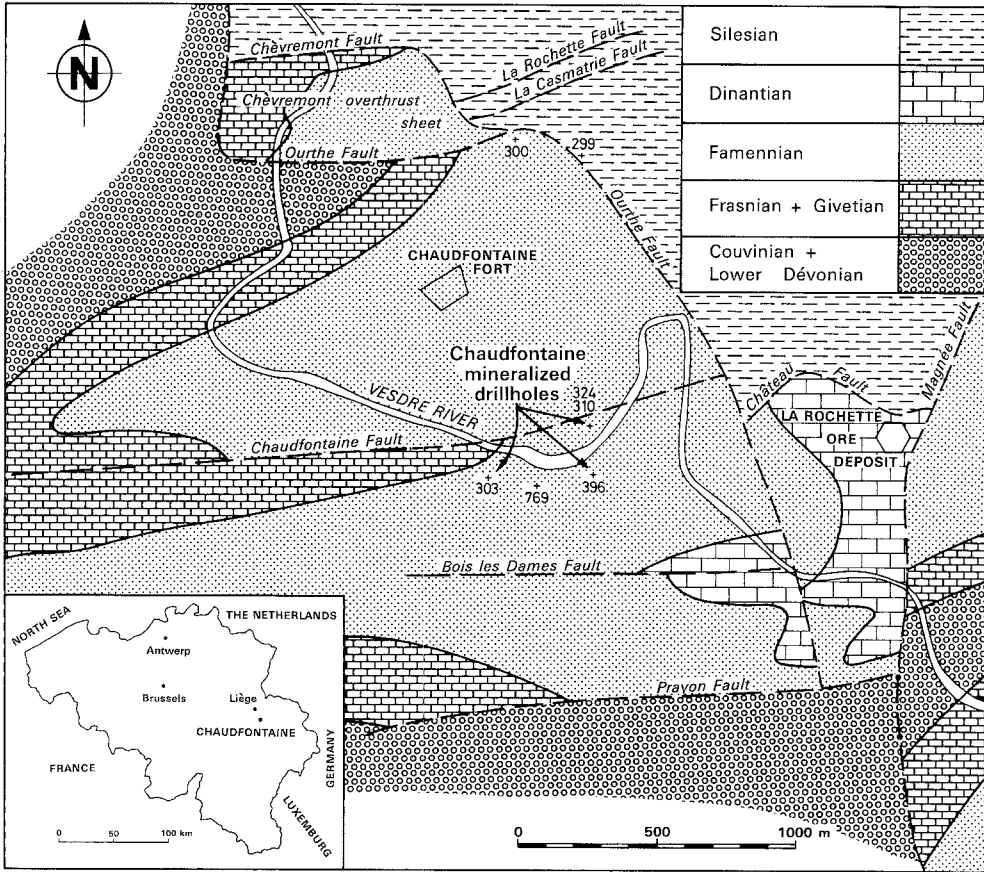


Fig. 1. Geological map of the Chaudfontaine area. The numbers correspond to the position of some drill holes (chosen among the deepest ones)

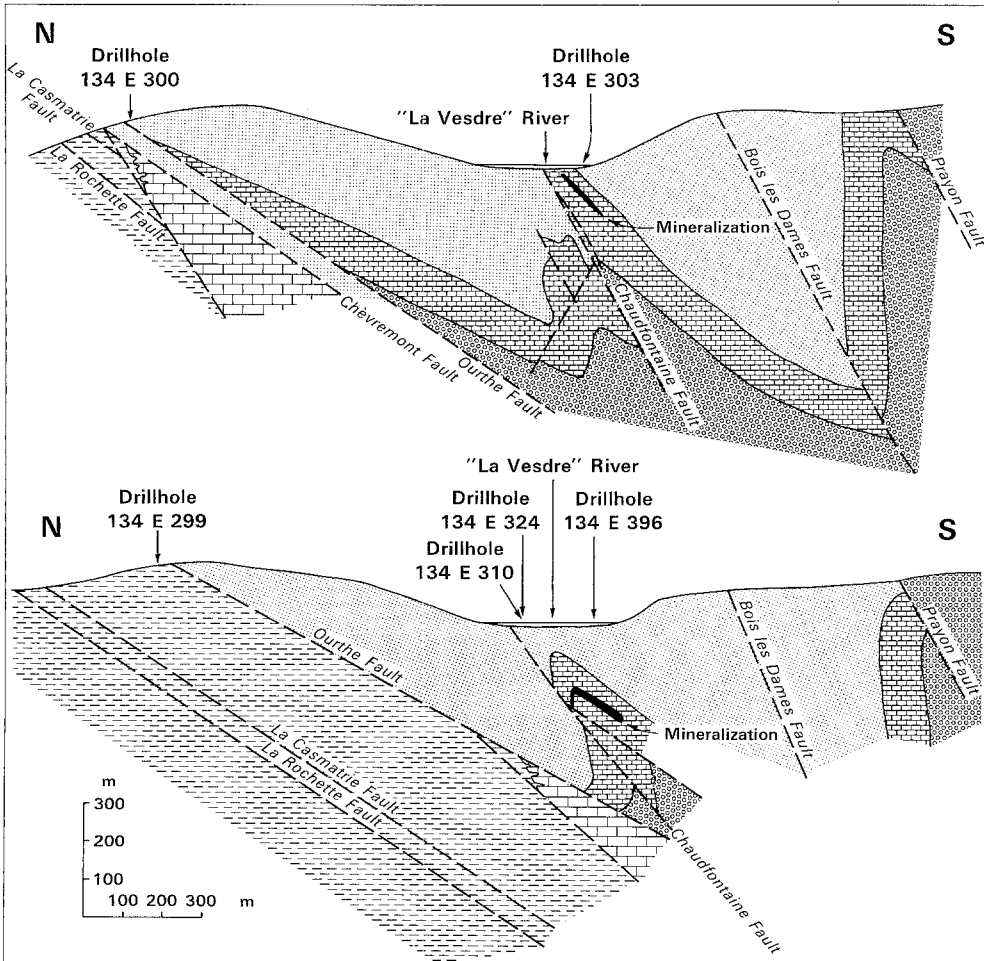


Fig. 2. Above, NS cross section through drill holes 134 E 300 and 303 (modified from Graulich 1967). The locations of these drill holes are plotted in Fig. 1. Below, NS cross section through drill holes 134 E 299, 310, 324, and 396 (modified from Graulich 1967 and Graulich & Vandeven 1978). The locations of these drill holes are plotted in Fig. 1. Same symbols as in Fig. 1

dominant. Some cm-sized calcite crystals are tabular in outline. Under the microscope, calcite and barite appear to be associated in aggregates with the same tabular habit. Thus, there appears to be lamellar intergrowth of barite and calcite. In some cases, even polymineral lamellae have been identified: one part being made up of calcite, the other of barite, with very sharp contacts between the two minerals. The hypothesis that the lamellar calcite is pseudomorphic after gypsum, or perhaps even more specifically after selenite in the case of the crystals a few cm in size, has been argued by Dejonghe (1986).

The matrix of the ore is complex. It consists of a mixture of black chert, often predominant, and argillaceous limestone with variable amounts of dolomite. Sedimentary breccias are also abundant. The contacts between the mineralized beds and the barren layers are always parallel to bedding. Sometimes, the contacts are very sharp, but they may also be gradual with continuous variation in the shape and size of the barite crystals.

The hanging wall of the orebody consists of light-gray nodular limestones (the argillaceous matrix of which is very important) interbedded with irregular layers of green and red shales. In the footwall, gray and black limestones (0.20 m up to 20 m thick), sometimes brecciated, cap a red bioherm and thin red and green shaly layers.

About 1,250 m east of the mineralized drill holes of Chaudfontaine at the border between the communities of Chaudfontaine and Forêt (at a place called "La Rochette") there is a small vein-type deposit (Fig. 1) described by Dejonghe et al. (1985). The Chaudfontaine and La Rochette ore deposits, though of different types, present many analogies with respect to their mineralogical assemblages. Indeed, both deposits contain bravoite and important amounts of barite and quartz, three minerals which are only present in small amounts in the other vein-type deposits of the district. Furthermore, it is at Chaudfontaine that the warmest thermal springs of Belgium (36°C) rise up again. On the basis of these facts, Dejonghe & Jans (1983, p. 21) have put forward the hypothesis that a genetic link could perhaps exist between the Chaudfontaine and the La Rochette deposits.

Analytical results

Detailed isotopic results are listed in the Appendix.

S isotopic compositions of barite

Investigations in S isotope geochemistry have shown that modern seawater has a uniform isotope composition (Ault & Kulp 1959). This is due to the rapid mixing rate of the waters which flow into the oceans. Furthermore, the presence of evaporites in sedimentary sequences of all ages, from the Precambrian to Recent, attests to the persistence of sulfates in oceanic waters. It is thus possible to trace the evolution of the S isotopic composition of ancient oceans by studying evaporites of different ages. Figure 3 shows the $\delta^{34}\text{S}$ variation curve of marine sulfates from the end of the Precambrian to modern times.

The S isotopic compositions of nine barites from drill hole 134 E 396 are presented in Appendix A. Rye's results (*, Appendix A) are taken from Dejonghe et al. (1982a); they are in perfect agreement with the four analyses of Lé-

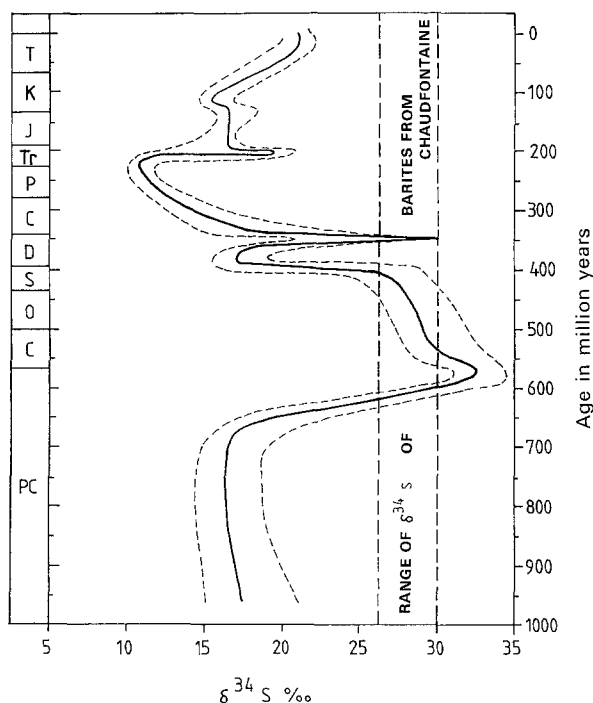


Fig. 3. Range of S isotopic composition of the barites from Chaudfontaine plotted on the $\delta^{34}\text{S}$ evolution curve for marine sulfates versus geological time. The continuous line represents the best estimate of the average S isotopic composition. The area between the dashed lines gives the range of dispersion of the data (adapted from numerous authors mentioned in Routhier 1980). The vertical dashed lines indicate the range for the Chaudfontaine barites

tolle (**, Appendix A), which are reported here for the first time. The values range 26.1–30.5 per mil, relative to the Canyon Diablo troilite. It appears that the depositional environment was sulfate dominant, and therefore, the $\delta^{34}\text{S}$ of the barites reflects the total S in the parent solution.

The comparison between these data and the $\delta^{34}\text{S}$ variation curve of marine sulfates versus time (Fig. 3) indicates that the Chaudfontaine samples are in the range of Devonian and pre-Devonian seawater sulfates. As the Chaudfontaine deposit is hosted in rocks of Frasnian age, its emplacement age is either Frasnian or younger. From these two sets of conditions, we can conclude that only a Frasnian age (i.e., around 355 Ma) is compatible with the S isotope data. Thus, the barites of Chaudfontaine plot exactly on the Devonian peak of the $\delta^{34}\text{S}$ variation curve of marine sulfates and the sedimentary origin of the Chaudfontaine mineralization is more firmly implied.

The simplest genetic interpretation is that the sulfate sulfur of the barites was derived from the Frasnian seawater either directly from the ocean or indirectly from solutions which dissolved marine sulfates deposited in an adjacent sedimentary basin. This is supported by the identification of pseudomorphs after gypsum and anhydrite in layers interbedded between the barite layers (Dejonghe 1985, 1986). Moreover, anhydrite is present at the same stratigraphic level as that of the Chaudfontaine mineralization in the Soumagne drill hole situated at about 8 km northeast of the Chaudfontaine drill holes (Graulich 1977).

The slight variations in the $\delta^{34}\text{S}$ values could be due to

1. local variation in the water composition in a restricted basin in which the mineralization was deposited (i.e., a la-

goon with temporary connections to the open sea or a lagoon occasionally fed by continental waters),

2. the mixing of two sources with isotopically distinct sulfur, and

3. variations in the intensity of bacterial reduction.

The metallotects related to the Chaudfontaine mineralization have been specified by Dejonghe (1985). At the end of the Frasnian, Chaudfontaine was located near a high on the flank of a main ridge (the so-called Booze-Le Val Dieu ridge). Many geologists think that this ridge was separated from the continent (the Brabant massif). The influence of continental surficial water as hypothesized by (1) was thus probably not very important. The question of the existence of Frasnian volcanic activity, eventually responsible for an additional S source (2), has been discussed by Dejonghe (1985, p. 212). However, indications to support this assumption are scarce. In fact, the depositional site of the Chaudfontaine mineralization corresponded to small shallow basins formed on the irregular surface of a biostromal formation. These basins were temporarily isolated as indicated by pseudomorphs after gypsum and anhydrite. In such evaporitic and mainly subevaporitic environments, Perthuisot (1980, p. 229) has emphasized the proliferation of organisms as well as their high mortality rate. Bacterial reduction of sulfates could thus play an important role. Therefore (3) is favored by the authors in this case.

S isotopic compositions of galenas and pyrites

The S isotopic compositions of three galenas and three pyrites from drill hole 134 E 396 are given in Appendix A. Although the dispersion of the $\delta^{34}\text{S}$ values is rather great, all the values are close to zero and are very different from the $\delta^{34}\text{S}$ values of the barites (Appendix A).

It has been shown (see for example, Faure 1977, p. 414) that when isotopic equilibrium exists between two sulfides, the isotopic fractionation $\Delta^{34}\text{S}$ (difference of their respective $\delta^{34}\text{S}$) is related to their crystallization temperature (T, in K) according to the following relationship:

$$\Delta^{34}\text{S} = A \cdot 10^6 \cdot T^{-2}$$

where A is a constant. Using -1 per mil and -0.07 per mil for the $\delta^{34}\text{S}$ values for the Chaudfontaine galena and pyrite, respectively, and the value (1.319) of Sakai (1968) for the A constant, we obtain a temperature of 1,191 K ($=918^\circ\text{C}$).

This abnormally high temperature is in strong disagreement with the low depositional temperatures indicated by the fluid inclusions in the barites (Dejonghe et al. 1982 b). It presumably means that the galenas and the pyrites were not in isotopic equilibrium at the time of deposition. Such behavior often characterizes low temperatures of deposition (see for example, Sakai 1968 or Smith et al. 1977).

The $\delta^{34}\text{S}$ differences between sulfides and sulfates from the same ore deposit are systematic. Bacterial reduction of the sulfates is one of the main factors accounting for these differences. In fact, at temperatures below 50°C , which is the case of the Chaudfontaine ore deposit, bacterial reduction seems to be the only mechanism possible for sulfate-sulfide reduction (Hoefs 1987, p. 53). As a consequence of this process, the sulfides are lower in $\delta^{34}\text{S}$ by about 5–25 per mil (15 per mil as a mean) with respect to the contemporaneous seawater sulfate. Hartman & Nielsen (1969) have, however, detected variations of up to 62 per mil. In the case

of the Chaudfontaine deposit the differences in the $\delta^{34}\text{S}$ values between sulfates and sulfides (24.4 up to 33.9 per mil) are thus quite plausibly accounted for by bacterial reduction. This conclusion is also supported by (3) of the previous section.

C isotopic composition of calcites and limestones

Organic compounds of biogenic origin usually have $\delta^{13}\text{C}$ values in the range of -10 down to -50 per mil/PDB (average $\delta^{13}\text{C}$ value of -25 per mil/PDB) irrespective of the age and composition of the rock. In contrast, the $\delta^{13}\text{C}$ values of marine carbonates (of all ages) are always close to zero on the PDB scale, whereas freshwater carbonates have generally negative $\delta^{13}\text{C}$ values (relative ^{13}C depletion). This depletion has been related to the presence of CO_2 gas produced by plant respiration and by plant putrefaction in the soil. For more information on this subject see Faure (1977) or Hoefs (1987).

The $\delta^{13}\text{C}$ values of carbonates are thus potentially sensitive environmental indicators. However, the isotopic composition can be modified during diagenesis and/or metamorphism, making interpretation more difficult. In the case of the Chaudfontaine ore deposit, a diagenetic influence is possible, but a metamorphic influence can be ruled out.

C isotopic compositions have been determined for

- five white sparry calcites from layers interbedded with barite layers of drill hole 134 E 396. Analyses 195.58 (1), (2), and (3) correspond to three samples taken from the same calcite monocrystal, 5 mm apart;
- two limestones from a barren bank interbedded between mineralization layers of drill hole 134 E 396 (at depths of 208.20 m and 209.20 m);
- two Frasnian limestones sampled in the Lustin Formation at Trooz (near Chaudfontaine). These samples (Z136 and Z252) were also used for the Sr isotope determinations (see below). Analysis Z136 has been repeated.

The results are presented in Appendix B. The $\delta^{13}\text{C}$ values of the eight sparry calcites vary from -1.11 to -3.55 per mil, and those of the five limestones from $+1.12$ to -2.12 per mil. It is thus clear that the C of these samples is not of organic origin. The $\delta^{13}\text{C}$ values of sparry calcites and limestones are close to zero of the PDB scale. However, the mean of the eight sparry calcites (-2.0 ± 0.6 per mil) is slightly lower than the mean of the five limestones (-0.024 ± 1.33 per mil). On the one hand, the sparry calcites show a discrete negative shift in the direction of typical $\delta^{13}\text{C}$ values for freshwater carbonates. But on the other hand, they are not characterized by broad $\delta^{13}\text{C}$ variations as are freshwater carbonates. Since calcite is pseudomorphic after gypsum (Dejonghe 1986), the slight $\delta^{13}\text{C}$ variations between the sparry calcites and the limestones could be related to sedimentary facies and/or diagenetic evolution.

O isotopic compositions of calcites, limestones, barites, and cherts

Oxygen isotopic fractionations between coexisting minerals can give useful information on their crystallization temperature. Indeed, when two phases have crystallized at equilibrium in the same reservoir, the differences of their $\delta^{18}\text{O}/\text{SMOW}$ is a function of temperature. This relationship

is expressed by the following equation (see for example, Faure 1977, p. 352):

$$\delta_1 - \delta_2 \cong 1,000 \ln \alpha_{12} = A \cdot 10^6 \cdot T^{-2} + B,$$

where

- α_{12} corresponds to the isotope fractionation factor between the phases 1 and 2,
- T is the absolute temperature (K), and
- A and B are constants.

The isotopic fractionation factors between calcite and water have been determined down to 0°C (O'Neil et al. 1969), but those between quartz and water are not known below 200°C (Clayton et al. 1972). Nevertheless, we know that the numerical values of the O isotopic fractionation factors for water-mineral equilibrium are always higher for quartz than for calcite at a given temperature (see for example, Faure 1977, p. 353); this is confirmed by the cherts and calcites of Chaudfontaine (Appendix C).

By applying the above equation to the quartz-water system (with $A=3.38$ and $B=-3.40$ from Clayton et al. 1972, valid in the T range of 200°–500°C) and to the calcite-water system (with $A=2.78$ and $B=-3.40$, from O'Neil et al. 1969, valid in the T range of 0°–800°C), we obtain

$$1,000 \ln \alpha_{QW} = 3.38 \cdot 10^6 \cdot T^{-2} - 3.40$$

$$1,000 \ln \alpha_{CW} = 2.78 \cdot 10^6 \cdot T^{-2} - 3.40$$

By subtracting the second equation from the first, we have

$$1,000 \ln \alpha_{QW} - 1,000 \ln \alpha_{CW} = 0.60 \cdot 10^6 \cdot T^{-2}.$$

This can be approximated as (see for example, Faure 1977, p. 355):

$$\delta_Q - \delta_C = 0.60 \cdot 10^6 \cdot T^{-2},$$

where δ_Q and δ_C refer to the $\delta^{18}\text{O}$ values of quartz and calcite.

We can calculate the temperature of oxygen isotopic equilibration for the Chaudfontaine ore deposit assuming that the quartz (chert) and the calcite have equilibrated their oxygen with the same reservoir and that the first equation above can be extrapolated below 200°C. For δ_Q and δ_C we have chosen the arithmetic means of the numerical values shown in Appendix C, i.e., 28.9 and 21.64 per mil, respectively. We have

$$(28.90 - 21.64) = 0.60 \cdot 10^6 \cdot T^{-2},$$

$$T = 287 \text{ K} = 14^\circ\text{C}.$$

The same reasoning with quartz (chert) and limestone gives $T = 293 \text{ K} = 20^\circ\text{C}$. These results are in perfect agreement with the fluid inclusion data.

The interpretation of the oxygen isotopic composition of barite is more complex. O and S isotopic equilibria in the $\text{BaSO}_4\text{-HSO}_4\text{-H}_2\text{O}$ system of 110°–350°C have been investigated by Kusakabe & Robinson (1977). When applying their data to the barite-quartz and the barite-calcite systems, negative temperatures (in °C) were obtained. Several explanations can be proposed, i.e.,

1. extrapolation of their data below 110°C is not valid,
2. isotopic equilibrium between barite and other solid phases has not been reached, or
3. barite and other solid phases have precipitated from different solutions.

The oxygen isotopic compositions of both Chaudfontaine calcites and Frasnian limestones are quite close, i.e., 20.8–23.3 per mil and 20.1–23.1 per mil, respectively. Slight variations are however present. Among the factors responsible for such variations, the salinity of the seawater is probably one of the most important. Indeed, a difference of salinity of 1 per mil implies a differences in $\delta^{18}\text{O}$ of 0.29 per mil (Faure 1977, p. 337). Since the role of salinity is enhanced in evaporitic environments, the ^{18}O isotopic variations are possible on the scale of a single crystal. This is illustrated in Appendix C where 3 samples of the same sparry calcite crystal (pseudomorphic after gypsum) from a depth of 195.58 m and 5 mm apart in the crystal show differences in $\delta^{18}\text{O}$ up to 1.80 per mil.

Sr isotopic compositions of barites, calcites, and limestones

Sr isotopic compositions have been determined for nine barites from drill hole 134 E 396. Furthermore, two white sparry calcites from layers interbedded between the barite and calcite are coeval. The Sr isotopic composition of two Frasnian limestones from the Lustin Formation (sampled at Trooz and selected on the basis of their high CaO content, i.e., low argillaceous content) have also been determined (in the logs published by Dejonghe 1985, p. 326ff., these samples are registered under numbers Z136 and Z252). Moreover, in order to assess the hypothesis of a genetic relationship between the Chaudfontaine sedimentary ore deposit and the adjacent La Rochette vein-type deposit, a barite from the La Rochette lode has also been analyzed.

The analytical results on Sr isotope are reported in Appendix D. As barites are insoluble, the Sr was partly washed out by a HF-HClO_4 acid mixture. This procedure was repeated twice for two samples (from drill hole 134 E 396, at depths of 200.85 m and 210.75 m) in order to check the reproducibility of the method. Calcites and limestones were dissolved in hydrochloric acid. The $^{87}\text{Sr}/^{86}\text{Sr}$ isotopic ratios measured by a Finnigan Mat 260 mass spectrometer have been normalized for a $^{88}\text{Sr}/^{86}\text{Sr}$ ratio of 8.3752. The isotopic composition of the standard, NBS 987, determined under the same analytical conditions is 0.71024 ± 0.00002 (2σ).

The results show that all the samples from the Chaudfontaine ore deposit have very similar Sr isotopic compositions. The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios are 0.71119 ± 0.00018 for the nine barites and 0.71137 ± 0.00022 for the two calcites, respectively. These observations indicate

1. that the barites are isotopically homogeneous, whatever their stratigraphic position is, and
2. that the barites and associated white sparry calcites or the mineral from which the latter derives (gypsum) are coeval and have crystallized from the same solution.

The barite from the La Rochette vein-type deposit differs substantially from the barites from the Chaudfontaine sedimentary ore deposit. Both Sr content and Sr isotopic composition are higher. This means that a direct lineage between the two ore deposits is questionable. Either the sources of their Sr (and probably Ba) are different or the La Rochette Sr (and Ba) partly derives from the Chaudfontaine deposit and partly from another source.

By using pure marine carbonate rocks, Burke et al. (1982) have established the variation in the Sr isotopic composition of seawater during the Phanerozoic (Fig. 4). The Sr

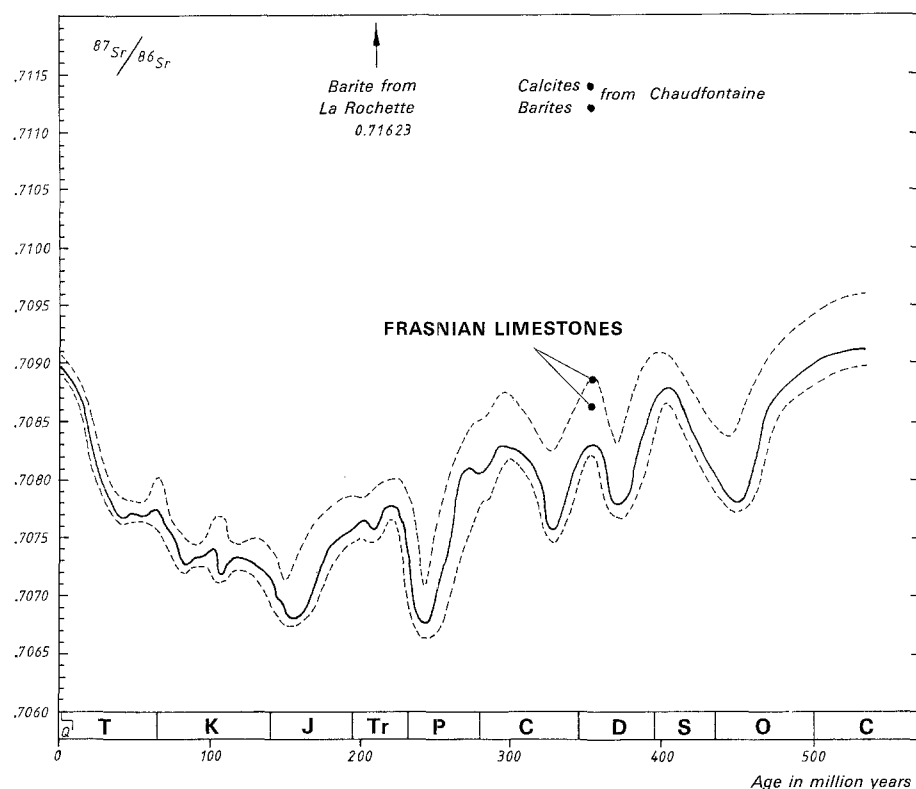


Fig. 4. Position of the barites and calcites from Chaudfontaine, of the barite from La Rochette, and of Frasnian limestones from Trooz on the $^{87}\text{Sr}/^{86}\text{Sr}$ evolution curve of seawater during the Phanerozoic. The continuous line corresponds to the best estimate of the average Sr isotopic composition. The area between dashed lines gives the range of dispersion of the data (adapted from Burke et al. 1982)

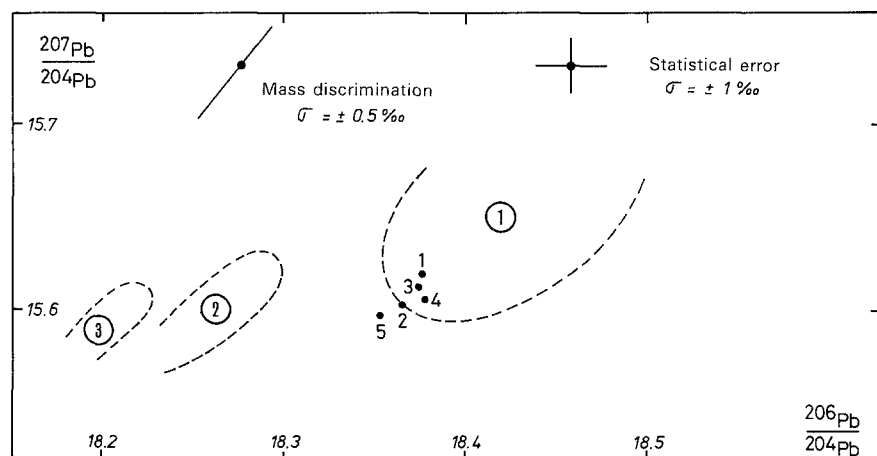


Fig. 5. Pb isotopic compositions of galenas from the Chaudfontaine ore deposit (data points 1–5). The dashed lines indicate three groups which correspond to most of the data of approximately 50 other Belgian mineral occurrences (adapted from Dejonghe et al. 1982 and Cauet et al. 1982)

isotopic compositions of the Frasnian limestones from Trooz (see Appendix D and Fig. 4) fit very well with those of the Frasnian portion of the curve. However, both barites and calcites from Chaudfontaine have much higher $^{87}\text{Sr}/^{86}\text{Sr}$ ratios. These results imply that the Sr (and probably also the Ba) of the Chaudfontaine ore deposit was not derived – at least not entirely – from the seawater and that a large proportion, which is, however, impossible to determine, must have been derived from a different source. This second and more important source of Sr as well as Ba could be surficial or deep leaching of a continental crust either rich in feldspars or rich in shales.

Pb isotopic compositions of galenas

The Pb isotopic compositions of five galenas from the Chaudfontaine ore deposit have been published by Dejonghe et al. (1982a). The five galenas have similar Pb isotopic compositions (18.34–18.39 for $^{206}\text{Pb}/^{204}\text{Pb}$, 15.61–15.63 for $^{207}\text{Pb}/^{204}\text{Pb}$, and 38.32–38.42 for

$^{208}\text{Pb}/^{204}\text{Pb}$). The mineralization encountered by the drill holes can therefore be considered to be isotopically homogeneous. On the other hand, Cauet et al. (1982) and Cauet (1985) have demonstrated that the Pb isotopic compositions of about 50 Pb-Zn mineralizations of various genetic types occurring in Belgium fall within a narrow range (18.18–18.48 for $^{206}\text{Pb}/^{204}\text{Pb}$, 15.57–15.68 for $^{207}\text{Pb}/^{204}\text{Pb}$, and 37.94–38.65 for $^{208}\text{Pb}/^{204}\text{Pb}$). In the $^{207}\text{Pb}/^{204}\text{Pb}$ versus $^{206}\text{Pb}/^{204}\text{Pb}$ diagram (Fig. 5), three groups may however be distinguished. Group 1 represents the greatest amount of Belgian mineralizations as well as those with the largest tonnages. It corresponds to all the lodes of the Namur and Verviers synclinoria hosted in Devonian as well as Dinantian formations, a large number of the lodes of the Dinant synclinorium, and disseminated-type ore deposits hosted in the Frasnian dolomites of the Dinant synclinorium. The galenas of Chaudfontaine are localized at the lower limit of this group. Group 3, substantially less radiogenic, corresponds to some disseminated-type ore

deposits hosted in the Givetian and Frasnian dolomites of the Dinant and Verviers synclinoria. The small lodes hosted in the Couvinian and the Givetian formations of the southern limb of the Dinant synclinorium as well as small lodes hosted in the Lower Devonian of the Ardenne are intercalated between these two groups.

The Pb isotopic composition of the Chaudfontaine sedimentary ore deposit is thus not different from those of the vein mineralizations. This observation led Dejonghe et al. (1982) to assume that the Pb from all the Belgian mineralization could come from a similar source (consanguinity) and has undergone a complex evolution involving the sedimentary trapping of the metals and various steps of diagenetic and post-Variscan epigenetic remobilizations. During this complex history the Pb isotopic composition has not evolved very much (the Pb of the vein mineralizations being only a little more radiogenic than the neighboring syndiagenetic mineralizations).

Additionally, a comparison of the Pb isotopic composition of the galenas of the Belgian mineralizations with that of syndimentary pyrites led Cauet et al. (1982) to propose that only the Middle and Upper Devonian sediments could be considered as the main source of Pb for the Belgian Pb-Zn mineralizations.

Conclusions

Isotope geochemistry applied to the Chaudfontaine mineralization has permitted us to draw very interesting genetic conclusions.

The $\delta^{34}\text{S}$ values of the barites agree with those of marine sulfates of Upper Devonian age, implying a marine origin for the sulfur. Slight $\delta^{34}\text{S}$ differences between samples are thought to be due to variations in the intensity of bacterial reduction. The sulfur of the sulfides (i.e., galena and pyrite) very probably results from bacterial reduction of the sulfates of the mother solution. Galena and pyrite are not in isotopic equilibrium, which often occurs in low-temperature deposition.

The $\delta^{13}\text{C}$ values of the white sparry calcites do not support an organic origin for the carbon. C isotopic compositions of the calcites and Frasnian limestones are very similar. The slight $\delta^{13}\text{C}$ variations could be related to sedimentary facies or/and diagenetic evolution.

The white sparry calcites and the Frasnian limestones have comparable O isotopic compositions. Slight $\delta^{18}\text{O}$ variations are probably related to variations in seawater salinity. Crystallization temperatures deduced from O isotopic fractionation are low, i.e., in the range of 10° – 20°C , which agrees well with the barite fluid inclusion data and supports the hypothesis of low-temperature deposition.

Whatever their stratigraphic position, all barites and interbedded sparry calcites have similar Sr isotopic composition. The barites and the white sparry calcites, or the mineral from which they were derived (gypsum), are coeval and have crystallized from the same solution. The measured $^{87}\text{Sr}/^{86}\text{Sr}$ ratios for both minerals (clustering around 0.7112) are significantly higher than the Frasnian seawater ratio (around 0.7087) implying a preponderantly nonmarine origin for the Sr (and probably the Ba). A direct lineage between the Chaudfontaine sedimentary mineralization and the La Rochette vein-type ore deposit appears unlikely.

The similarity of the Pb isotopic compositions of the Belgian Pb-Zn sedimentary and vein-type ore deposits suggests a common source for the Pb which is mainly found in the sediments of Middle and Upper Devonian age.

Finally, the isotopic data allow us to specify the genesis of the Chaudfontaine mineralization. Field observations have indicated that at the end of the Frasnian the Chaudfontaine area lay near a high on the southern flank of the Booze-Le Val Dieu ridge (Dejonghe 1985; Cnudde et al. 1986). This high probably emerged after the deposition of the second *Phillipsaeraea* biostromal unit of the Aisemont Formation, the top of which is very irregular. Consequently, small shallow pools were temporarily isolated from the open sea and evolved evaporitic conditions. Sulfate solutions were thus present in substantial amount in these small shallow pools. In such environments, proliferation of organisms

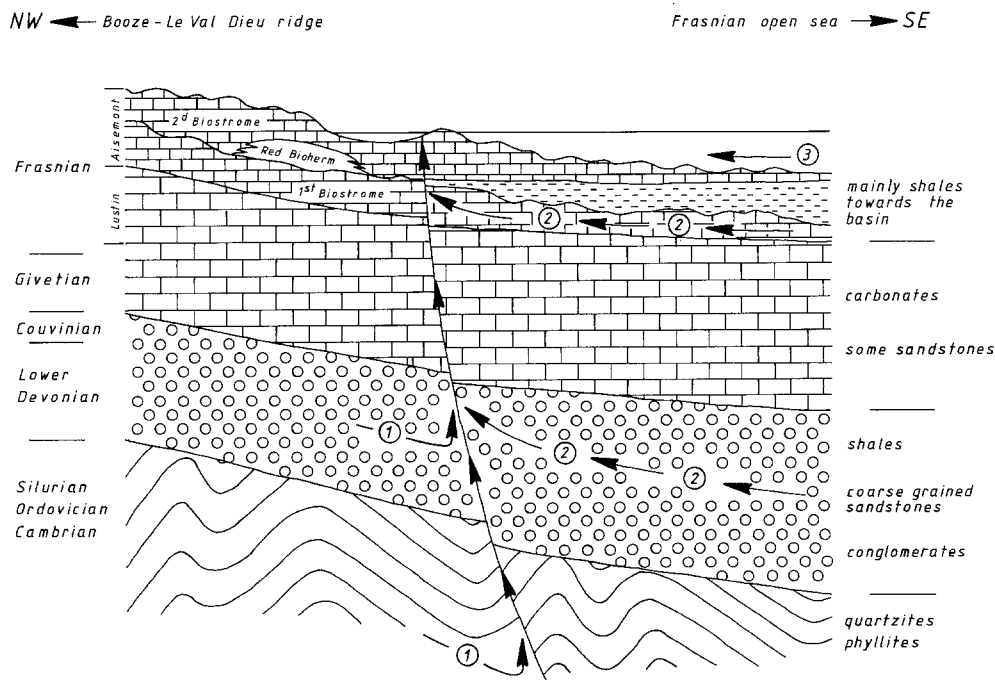


Fig. 6. Landscape pattern of the Chaudfontaine area at the end of the Frasnian and hypotheses concerning the source of the metals. 1, continental meteoric waters; 2, connate waters; 3, marine volcanic activity

is high, as is their mortality. Thus, bacterial reduction of sulfates can play an important role. If metals were available, very favorable conditions for their precipitation would have existed.

Though the Chaudfontaine ore trap is relatively well defined, the source of the metals is less obvious. In any event, it appears that precipitation could have occurred during the mixing of two different solutions (one bringing the S, the other bringing the metals). The possibility of two solutions is supported by the isotopic data indicating that the S is of marine origin whereas the Sr and Ba are of nonmarine origin. The following three hypotheses may be put forward (Fig. 6):

1. The metals have been carried out by continental meteoric water making a complex underground journey before rising again to the surface (path 1). During this journey, the solutions, possibly modified by contact with evaporites at some stage in their evolution, leached the metals from the formations through which they flowed.

2. The metals have been transported by connate waters expelled during the compaction of a subsiding basin (path 2).

Appendix. List of isotopic results

A S isotope composition of barites, galenas, and pyrites (barite analyses, * Rye, USGS, Denver; ** Létolle, Univ. Paris 6; galena and pyrite analyses, Boulègue and Létolle, Univ. Paris 6)

Nature of mineral	Depth (m) in drill hole 134 E 396	$\delta^{34}\text{S}/\text{Canyon Diablo}$ (per mil)
barite	194.95	27.0 (*)
barite	195.50	27.5 (*)
barite	200.80	30.5 (**)
barite	201.50	28.5 (**)
barite	201.90	30.1 (*)
barite	204.55	28.0 (**)
barite	207.00	28.1 (*)
barite	207.50	26.1 (*)
barite	209.85	26.6 (**)
galena	200.05	-0.5
galena	201.68	-3.4
galena	209.80	0.9
pyrite	194.42	1.7
pyrite	198.00	-3.1
pyrite	204.75	1.2

B C isotopic composition of sparry calcites and Frasnian limestones (analyses by Létolle, Univ. Paris 6)

Nature of mineral or rock	Depth (m) in drill hole 134 E 396 or sample no.	$\delta^{13}\text{C}/\text{PDB}$ (per mil)
calcite	195.58	-1.96
calcite	195.58 (1)	-1.11
calcite	195.58 (2)	-1.32
calcite	195.58 (3)	-1.87
calcite	195.90	-3.55
calcite	196.05	-2.49
calcite	196.40	-2.52
calcite	202.85	-1.18
limestone	208.20	+0.85
limestone	209.20	-2.12
limestone	Z 136 (1)	+1.12
limestone	Z 136 (2)	+1.10

Their natural NaCl-bearing composition may also have been reinforced by contact with evaporites. They flowed, then rising up through permeable formations (e.g., biostromes or sandstones) up to the margins of highs or to the shoreline. The metals may have been released from the clay minerals or leached from the feldspars contained in the sandstone formations (e.g., the arkosic horizons of the Lower Devonian).

3. A supply of metals linked with marine volcanic activity during the Frasnian cannot be completely ruled out. Traces of volcanism have been identified by Lacroix (1987) in the Frasnian of the Namur synclinorium, but not at the same stratigraphic level as the Chaudfontaine mineralization.

It is difficult to choose or to reject any one of these hypotheses even if arguments in favor of hypothesis 3 are as yet scarce. Hypotheses 1 and 2 are equally likely. For both, the source of metals is to be found in the sedimentary country rocks. For both, the brines have been brought to the site of deposition along active fault drains, which were also probably responsible for the structural pattern of the Chaudfontaine area (high).

C O isotopic composition of cherts, sparry calcites, barites, and Frasnian limestones (chert analyses by Boulègue and Fouillac, Univ. Paris 6; other analyses by Létolle, Univ. Paris 6)

Nature of mineral or rock	Depth (m) in drill hole 134 E 396 or sample no.	$^{18}\text{O}/\text{SMOW}$ (per mil)
chert	198.00	31.1
chert	198.63	28.2
chert	205.15	27.4
calcite	195.58	20.98
calcite	195.58 (1)	23.31
calcite	195.58 (2)	22.20
calcite	195.58 (3)	21.51
calcite	195.90	20.65
calcite	196.05	22.03
calcite	196.40	21.62
calcite	202.85	20.80
limestone	208.20	22.35
limestone	209.20	20.43
limestone	Z 136 (1)	23.24
limestone	Z 136 (2)	23.32
limestone	Z 252	20.14
barite	200.80	13.20
barite	201.50	12.20
barite	204.55	14.40
barite	209.85	12.70

D Sr isotopic compositions of barites, sparry calcites, and Frasnian limestones (analyses by Demaiffe, Univ. Libre Bruxelles)

Nature of mineral or rock	Depth (m) in drill hole or sample no.	$^{87}\text{Sr}/^{86}\text{Sr}$
Chaudfontaine (drill hole 134 E 396)		
barite	193.55	0.71170
barite	194.70	0.71123
barite	195.25	0.71098
barite	197.00	0.71092

(D continued overleaf)

D Sr isotopic compositions of barites, sparry calcites, and Frasnian limestones (analyses by Demaiffe, Univ. Libre Bruxelles) (continued)

Natural of mineral or rock	Depth (m) in drill hole or sample no.	$^{87}\text{Sr}/^{86}\text{Sr}$
barite	200.85 (1)	0.71133
barite	200.85 (2)	0.71128
barite	204.20	0.71111
barite	205.50	0.71123
barite	209.75	0.71105
barite	210.75 (1)	0.71118
barite	210.75 (2)	0.71119
calcite	196.15	0.71130
calcite	202.85	0.71144
<hr/>		
La Rochette		
barite	A8564	0.71623
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Trooz		
calcaire	Z 136	0.70887
calcaire	Z 252	0.70863

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