

**SULFUR ISOTOPES OF BARITE AND LEAD ISOTOPES OF  
GALENA FROM THE STRATIFORM DEPOSIT IN FRASNIAN  
CARBONATE AND SHALE HOST-ROCKS OF CHAUDFONTAINE  
(PROVINCE OF LIEGE, BELGIUM) <sup>1</sup>**

by

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(2 figures, 2 tables, 1 plate)

**ABSTRACT.**— Geological observations (Dejonghe, 1979) suggest a sedimentary origin to the Ba, Zn, Pb deposit of Chaudfontaine. This interpretation is supported by sulfur isotopic measurements of the barites. However, the lead isotopic data of the galenas are not obviously consistent with this conclusion. It is proposed to attribute a common source for Ba, Zn and Pb for most of the deposits of the Namur-Herve district (vein-type deposit included).

**RESUME.**— Sur base d'observations géologiques, Dejonghe (1979) a attribué une origine sédimentaire au gisement Ba, Zn, Pb de Chaudfontaine. Cette hypothèse est confirmée par des mesures isotopiques du soufre de 5 échantillons de barite. Cependant, l'interprétation des isotopes du plomb de 5 galènes provenant du même gisement est moins évidente. Afin de concilier les données isotopiques de tous les gisements belges, il est proposé d'attribuer une source commune pour le Ba, Zn et Pb de la plus grande partie des gisements, filoniens ou non, du synclinorium de Herve.

## 1. INTRODUCTION

The Chaudfontaine mineral deposit (Graulich, 1967 ; Dejonghe, 1979) is hosted in rocks of Frasnian age, at the transition zone where a carbonate formation grades to a shaly formation. More specifically, it occurs in a back-reef environment, very close to red bioherms. The deposit does not crop out and has not been mined. It has only been intersected by 3 drillholes and therefore knowledge of its shape and composition is only fragmental. The mineralization is predominantly barite and marcasite or pyrite. Sphalerite is also relatively abundant and galena occurs as sparse disseminated patches. Chalcopyrite and bravoite are very rare and only visible under the microscope. Present are sedimentary fabrics (including barite and, sometimes, sphalerite crystals) some of which are true geopetal fabrics (rhythmic pattern of layering of barite, sphalerite and barren sediments ; barite dm-crystals floors ; baritic filling sediments above barite dm-crystals floors ; levelling of relief irregularities of the water-sediment interface by baritic layers ; load casts ; slumping associated with intraformational breccias draping around isolated barite crystals ; resedimentary lamellar barite cm-crystals). Furthermore owing to its clear non-tectonical control, its similar stratigraphical position in the 3 drillholes separated from each other by several hundred meters,

its paleogeographical position in a restricted marine environment and the absence of any volcanic activity in the vicinity, the Chaudfontaine deposit appears to be classified as a sedimentary deposit. From geological observation, there is no obvious argument against this interpretation (e.g., no mineralized cross-cutting veins).

The confirmation of this statement is the presence at the same stratigraphical level of mineralized occurrences in 3 drillholes distributed on a distance of more than 100 km (barite at Bolland ; galena at Booischoot ; pyrite, sphalerite and galena at Heibaart (Loenhout) (Dejonghe, 1979).

However, no Zn, Pb, Ba sedimentary deposit has ever been previously mentioned in the main metallurgical district of Belgium (the so-called Namur-Herve district). Indeed, this district, with a Zn + Pb cumulate production of 1.25 miot of metals, has only been mined

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for hydrothermal vein-type deposits. This discovery of the Chaudfontaine deposit may thus have important economic as genetic implications.

The purpose of this study is to confirm the sedimentary origin of the Chaudfontaine deposit and to determine its relationship to the vein-type deposits. Sulfur isotopes of barite and lead isotopes of galena have been measured. The results are interpreted in the light of the regional geologic constraints.

## 2. SULFUR ISOTOPE GEOCHEMISTRY OF BARITES

### 2.1.- GENERAL CONSIDERATIONS

Studies have shown that modern sea-water has a remarkably uniform sulfur isotopic composition. Indeed, rapid mixing of the ocean effectively provides an infinitely large sulfate reservoir of constant isotopic composition. Furthermore, evaporite deposits in rocks younger than Late Precambrian attest the long term presence of sulfate in oceanic waters. Hence, it is possible to determine the isotopic composition of ancient seas by the study of fossil evaporites.

Figure 1 represents the variation of  $\delta^{34}\text{S}$  of marine sulfates from the Late Precambrian times up to now.

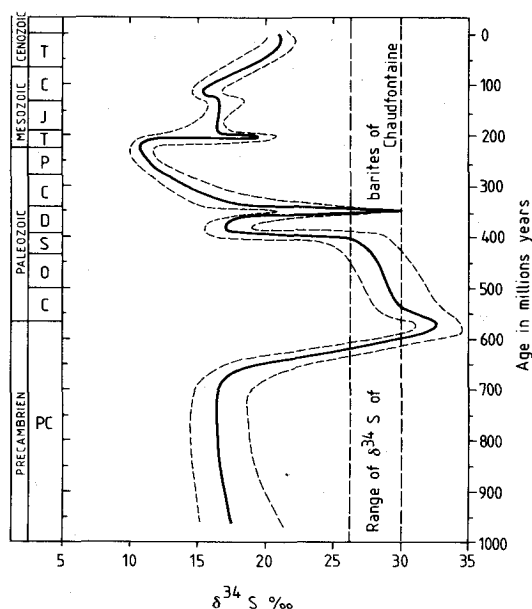


Figure 1

Strong line : mean variation of the sulfur isotopic composition of marine sulfates through geological time (adapted from Routhier, 1980, curve resulting of a compilation of various authors).

Dashed lines : range of dispersion of the data.

### 2.2. ANALYTICAL RESULTS

Five barite samples have been collected along the section of the ore deposit in drillhole 134E396. Barite occurs in a sedimentary rock consisting of a complex mixture of three components (siliceous, argillaceous and carbonate) among which the siliceous one (chert, or silicite sensu Teodorovich, 1958) often predominates.

Barite occurs in various forms :

- isolated and scattered subhedral crystals (lamellar or tabular shaped), sometimes with terminal crystal faces (euhedral crystals)
- aggregates of subhedral crystals more or less joined (often with  $120^\circ$  junctions)
- massive aggregates, often of large subhedral crystals
- spots of fine-grained anhedral aggregates.

Concerning the size of barite crystals, two populations may be distinguished (pl. 1) : one of crystals up to 1 cm length and the other of a length close to 10 cm (some crystals reach 20 cm length).

Table 1 gives a short description of the analyzed samples, their position in vertical drillhole 134E396 and their  $\delta^{34}\text{S}$  values relative to canon Diablo troilite. Isotopic sulfur investigations have been performed at the Isotope Geology Branch of the U.S. Geological Survey.

Table 1.- Sulfur isotopic composition of barites at the Chaudfontaine ore deposit

Number	Depth in vertical drillhole 134E396 (m)	Description of barites samples	$\delta^{34}\text{S}$ (‰)
1	194.90 195.000	centimetric to decimetric euhedral white barite crystals in a dark silicite	27.0
2	195.50	millimetric to centimetric lamellar white crystals randomly orientated in a dark silicite. Sparse sphalerite	27.5
3	201.90	massive barite aggregate made up of centimetric hypidiomorphic white barite crystals	30.1
4	207.000	same fabric as n <sup>o</sup> 3 but barite has a faint pinkish color	28.1
5	207.50	millimetric lamellar white barite crystals randomly oriented in a dark silicite. Also, some small anhedral barite and sparse millimetric sphalerite crystals.	26.1

### 2.3. INTERPRETATION

The  $\delta^{34}\text{S}$  values vary from 26.1 to 30.1. The middle sample, n<sup>o</sup> 3, has the highest value, from which the others decrease.

It appears from the samples that the system was sulfate dominant and, therefore, the  $\delta^{34}\text{S}$  of the barites reflects that of the total sulfur in the parent solution.

From the age variation curve of sulfur isotopic composition of marine sulfates (fig. 1), it appears that the  $\delta^{34}\text{S}$  of the barites of Chaudfontaine are in the range of pre-Devonian sea-water sulfates. As the Chaudfontaine deposit is hosted in rocks of Frasnian age (base of the Upper Devonian), its age of emplacement is either Frasnian, or younger. From these two sets of conditions, it follows that a Frasnian age (i.e. around 355 million years) is compatible with the  $\delta^{34}\text{S}$  values of the barites of Chaudfontaine.

This conclusion plots the barites of Chaudfontaine exactly on the Devonian peak of the  $\delta^{34}\text{S}$  variation of marine sulfates (fig. 1).

The simplest genetical interpretation is that the sulfate sulfur of the barite was derived from sea-water either directly from the ocean or from solutions which dissolved sea-water sulfate in the interior of the sedimentary basin. It should be pointed out that anhydrite is known in the upper part of the Frasnian (at the same stratigraphical level as Chaudfontaine), in the Soumagne drillhole, some kilometers east of Chaudfontaine (Graulich, 1977). This correlation has already stressed previously (Dejonghe, 1979).

The fact that the values appear to decrease systematically up and down from sample n° 3 could be interpreted

1. as a variation of the composition of the water of the restricted basin in which the ore deposit occurred (e.g. lagoon more or less open to the sea or lagoon more or less fed by continental waters)
2. as a result of the variations of intensity of the bacterial reduction
3. as a mixing of sulfur from two sources.

We will discuss the source of the barium after examining the results of the lead isotopic composition of the galenas.

### 3. LEAD ISOTOPE GEOCHEMISTRY OF GALENAS

The Belgian lead-zinc mineralizations have recently been the object of lead isotopes studies at the University of Brussels. Following the works of Pasteels and al. (1980), complementary research has been carried out (Cauet and al., 1981). The isotopic characteristics of the Chaudfontaine ore deposit will be integrated to these data. The latter may be summarized as follows.

The lead isotopic compositions obtained on fifty Belgian mineralizations fall in a narrow range of values ( $^{206}\text{Pb}/^{204}\text{Pb}$  from 18.1 to 18.5,  $^{207}\text{Pb}/^{204}\text{Pb}$  from

15.5 to 15.7 and  $^{208}\text{Pb}/^{204}\text{Pb}$  from 38.0 to 38.7). However various groups may be distinguished (fig. 2).

- A first group (1) is made up of all the vein mineralizations affecting the Devono-Dinantian of the Namur-Herve basins as well as some of the vein mineralizations of the mid-Devonian of the Dinant synclinorium. The clustering of the data seems to indicate that the metallogenic processes which govern these metal concentrations took place at a large scale.
- A second small group (2) is made up of the vein mineralizations of the Upper Couvinian and Givetien of the Dinant synclinorium. These could be the result of local processes.
- A third small group (3) is formed by mineralizations related to dolomitic levels from the Dinant and the Herve basins. The vein mineralizations of the low Devonian formations have more variable isotopic compositions.

Galena samples from Chaudfontaine ore deposit have been selected from drillhole 134E396. Galena occurs as disseminated patches of several millimeters in length, more or less confined to decimeter thick layers, and usually included in a siliceous sedimentary rock. Under the microscope, galena is also included in barite or more seldomly in sphalerite or pyrite but such galena has not been selected for isotopic investigations.

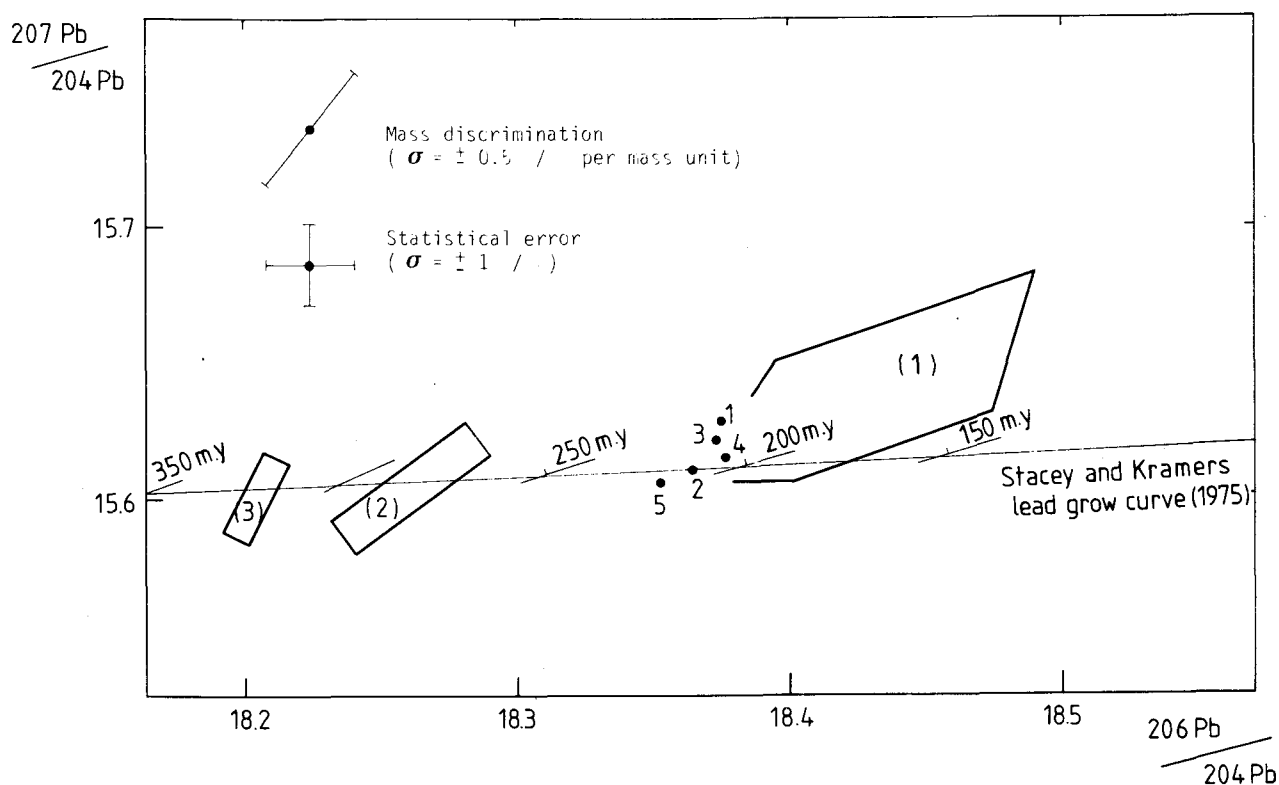
The lead isotopic results are shown in table II.

These isotopic ratios obtained on five galena samples are not substantially different. The mineralization crossed by the drillhole can therefore be considered as isotopically homogenous. In the 207/204 versus 206/204 lead diagram, the lead of these galena samples from the Chaudfontaine ore deposit is located at the limit of the group which includes all the vein mineralizations which affect the metallogenic district of the Herve basin (groupe 1). It is distinctly different from lead-zinc disseminations unrelated to veins (groupe 3). The lead of Chaudfontaine is not significantly different from that of the vein mineralizations; the lead from all these mineralizations would thus have a similar evolution in the crust and therefore would come from the same source (consanguinity).

The similarity between isotopic compositions of sedimentary and vein mineralizations is not clearly understood in view of the chronological and structural differences between these two types of mineralizations; the Chaudfontaine ore deposit is of Frasnian age, the vein ore deposits are post variscan. The lead isotope data on the Chaudfontaine ore deposit appears to be incompatible with the sedimentological characteristics and with

Table II.- Lead isotopic ratios of galenas of the Chaudfontaine ore deposit.

Number	Depth in vertical drillhole 134E396 (m)	Lead isotopic ratios		
		$^{206}\text{Pb}/^{204}\text{Pb}$	$^{207}\text{Pb}/^{204}\text{Pb}$	$^{208}\text{Pb}/^{204}\text{Pb}$
1.	194.45	18.37 <sub>6</sub>	15.63 <sub>0</sub>	38.41 <sub>5</sub>
2.	200.05	18.35 <sub>9</sub>	15.60 <sub>9</sub>	38.32 <sub>2</sub>
3.	203.50	18.37 <sub>6</sub>	15.62 <sub>1</sub>	38.36 <sub>7</sub>
4.	206.75	18.38 <sub>6</sub>	15.61 <sub>4</sub>	38.34 <sub>0</sub>
5.	210.90	18.34 <sub>1</sub>	15.60 <sub>5</sub>	38.36 <sub>6</sub>

Figure 2.- Lead isotopic ratios of galenas of the Chaudfontaine ore deposit reported in a  $^{207}/^{204}$  versus  $^{206}/^{204}$  lead diagram with lead isotopic ratios from other belgian mineralizations (Cauet and al., 1981).

the sulfur isotopic study of the barites of this ore deposit. Can the apparent divergencies be explained ?

The Stacey & Kramers lead evolution model (fig. 2) represents an average evolutive trend for crystal lead but does not necessarily conform to the evolution of lead in each specific case. The isotopic compositions of mineralizations are often the reflection of regional or possibly local features. The model ages does not always

correspond to the geological age and the difference may reach  $\pm 100$  m. y. This difference may explain the gap between the geological age of the Chaudfontaine ore deposit (355 million years) and the model age (200-250 million years).

The presence of a similar lead in the Chaudfontaine ore deposit and in the vein ore deposits from the Namur-Herve metallogenic district can be explained by

a common regional origin.

In order to explain the formation of these two types of mineralizations it is possible to consider the following processes :

- During the Devono-Dinantian : Atmosphéric alteration and leaching of the continent (Brabant massif and other emerged massifs). Pouring of the meteoric water charged with Pb, Zn, Ba, ... into the bordering sea. When the paleogeographic conditions corresponded to confined environments (lagoon for instance), enrichment of the geochemical background with these elements and locally sedimentary concentration (for instance at Chaudfontaine during the Frasnian).
- During the Permo-Trias : After the variscan orogenesis, development of transverse fractures (in most cases linked to the block-faulting tectonics of the Rhin graben). Opening of these fractures in their superficial parts due to local swelling (induced, for instance, by the movement or by the dissolution of underlying evaporites). Alimentation of the tectonic trap by leaching from the adjacent rocks.

In the proposed model, Pb, Zn, Ba ... have a common original source (consanguinity) but also a complex history : the continent enclosed a Pb, Zn, Ba, ... stock which was :

- displaced and deposited a first time at various periods during the Devono-Dinantian ;
- redeposited and deposited a second time during the Permo-Trias.

The origin of the pre Devonian elements (Pb, Zn, Ba, ...) remains unknown. The lead isotopic composition would not have practically evolved during this succession of phases of mobilisations and depositions (the lead from the veins is on average only slightly more radiogenic than those of Chaudfontaine).

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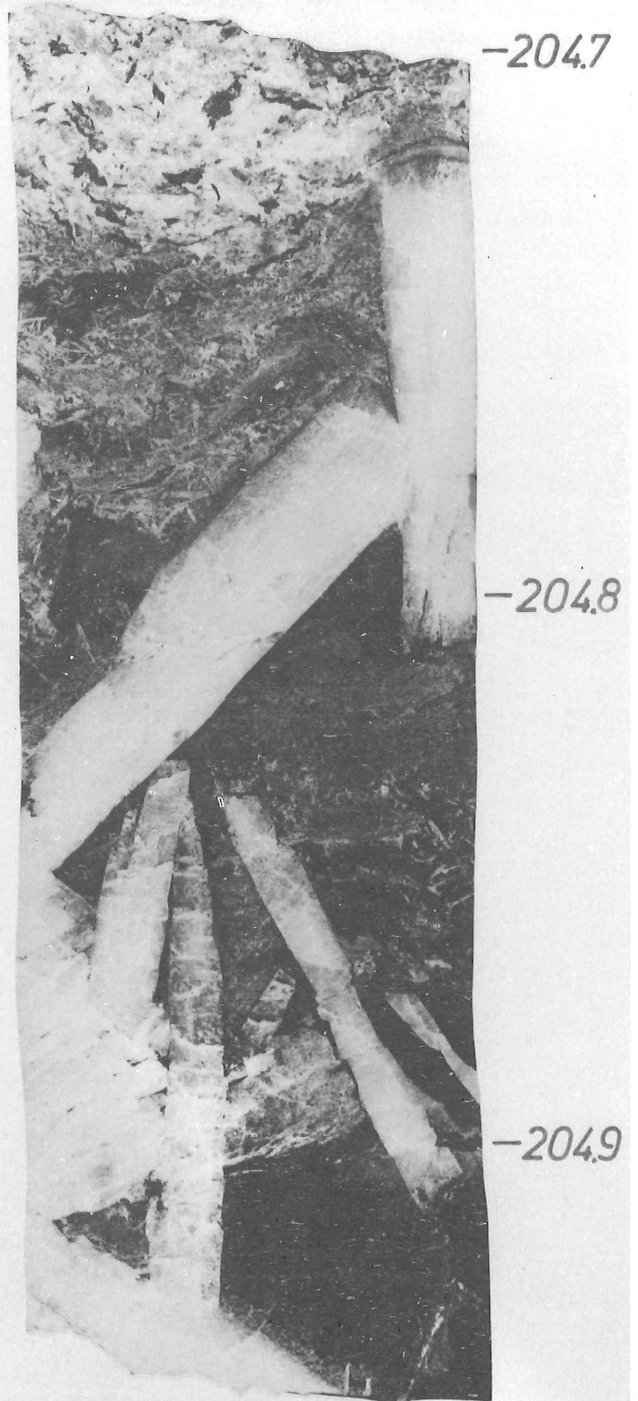
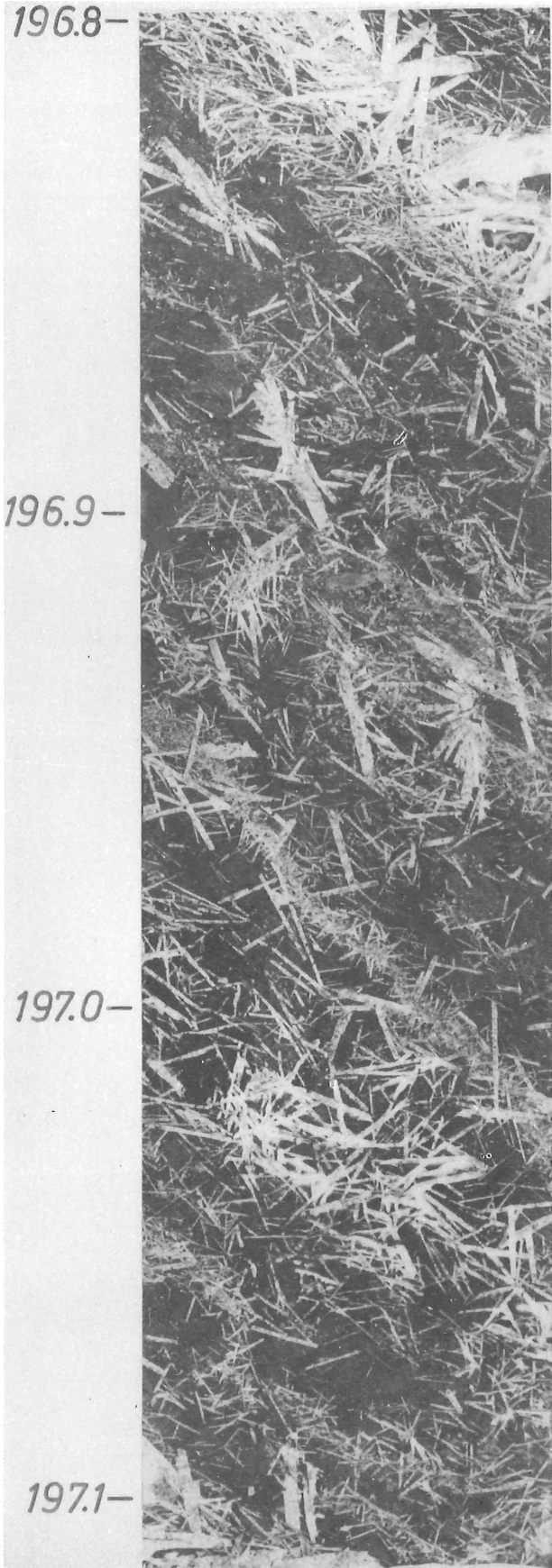
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**PLATE I**

Longitudinal sections through cores of vertical drillhole 134E396. Depths in meters are mentioned on the sides. Black groundmass is a complex mixture of three components (siliceous, argillaceous and carbonate). The two populations of barite crystals are represented : on the left, mm-cm crystals and on the right, dm crystals.



0 5 cm

A horizontal scale bar is located at the bottom center of the image. It consists of a black line with white segments, labeled '0' at the left end and '5 cm' at the right end.