

# Microbial control on the precipitation of amorphous iron oxide and carbonate modern deposits from the Cézallier hydrothermal springs, Massif Central, France

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Mineral deposits related to thermal springs are generally of the carbonate or silicate precipitation types. Numerous thermal waters have been studied worldwide for their extensive deposits (Italy, Iceland, New Zealand, USA). The occurrence of other deposit types, such as oxides, associated with hydrothermal activity are few. However, the almost pure manganese oxide deposit in Japan was recently studied to demonstrate the microbial mediation in the  $\text{MnO}_2$  precipitation through  $\text{Mn}^{2+}$  oxidation of Mn-rich waters [1]. The  $\text{CO}_2$ -rich thermal waters from the Massif-Central (France) are of special interest because both carbonate deposit and oxide precipitation generally occur [2]. As the pressure is released at the surface (bubbles of  $\text{CO}_2$ ) small red Fe-rich particles precipitate in the spring. With slower kinetics a layered carbonate travertine is formed farther downstream.

## Materials and methods

The seven thermomineral springs studied are located in the French Massif Central geothermal area, and more precisely, in the Cézallier and Limagne d'Allier areas where granitoids and gneisses are the two main lithologies encountered. The springs emerge with a low flow rate from the intensively fractured basement. The chemistry of these fluids is characterised by neutral pH (6–7), high  $\text{CO}_2$  concentrations with pressures ranging from 0.1 to 0.5 bar and high dissolved Na, Cl,  $\text{HCO}_3$  contents [2].

Water samples were collected after in situ pH, Eh, C and  $T^\circ\text{C}$  measurements. The water was immediately filtered through 0.45  $\mu\text{m}$  pore size filters and stored in polyethylene bottles for chemical analysis. Alkalinity was titrated immediately. Recently formed carbonate crusts and red particles of each spring were also sampled. The solids were dried, crushed (carbonate) and sieved at 70  $\mu\text{m}$ . The acidified water samples were analysed by atomic spectroscopy

and inductively coupled plasma emission mass spectrophotometry (ICP-MS). Anions were analysed by high pressure liquid chromatography. As the carbonate deposit can contain Fe-particles, the carbonated phases were specifically dissolved by gently acid leaching using cold HCl 0.2N. Iron oxide samples were dissolved by combined HCl/ $\text{HNO}_3$  attack. Atomic spectroscopy, X-ray fluorescence, and ICP-MS were used for the solid analyses.

## Physicochemical characterisation

The carbonate X-ray powder diffraction analysis indicates well-crystallised calcite with small amounts of aragonite and tridymite. The oxide diffractograms present two broad scattering bands around 1.5 and 2.6 Å as previously described for "2 lines" protoferrihydrite [3]. Traces of calcite are also present. X-ray absorption spectroscopy experiments permitted to describe the local structure of this hydrous ferric oxide mainly by edge sharing iron octahedra [4]. Although ageing proceeds up to 48 h at 150°C, no significant change is observed in the X-ray diffraction patterns. Pure hydrous ferric oxides evolve to a crystalline form in a few hours, whereas natural amorphous compounds are more stable and remain mainly disorganised. The Cézallier ferrihydrite precipitation occurs in a natural complex system, i.e. where foreign ions susceptible to interact with Fe ions are numerous and highly concentrated. The transformation of ferrihydrite to goethite or hematite is then significantly slowed, or even inhibited, by the coprecipitation and/or sorption of Si, Al, phosphates, As, etc.

## Thermodynamic calculations

The geochemical code EQ3NR [5] was used to calculate saturation indices and to determine the water speciation of each element depending on its

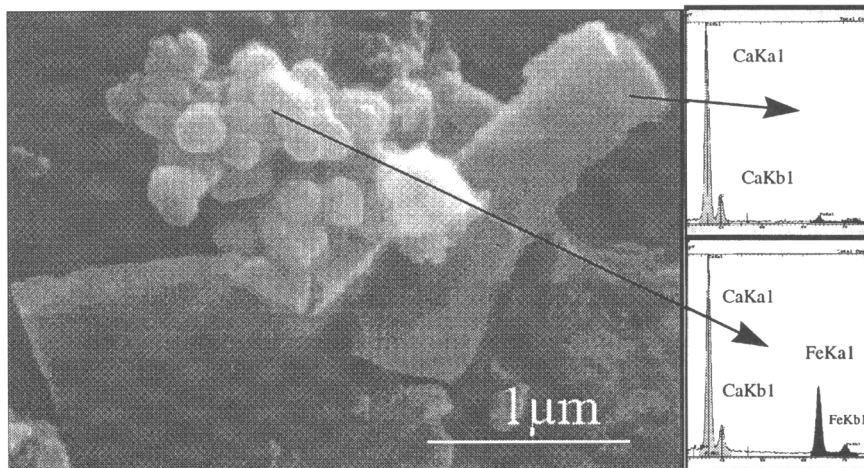


FIG. 1. SEM and Energy Dispersive Spectroscopy (20 keV) characterisation of the Cézallier carbonate deposit showing an iron enrichment on bacteria bodies with respect to calcite crystals.

concentration and on the ligand concentration ( $\text{HCO}_3^-$ ,  $\text{CO}_3^{2-}$ ,  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{OH}^-$ , etc). The minimum and maximum Saturation Index values [minSI, maxSI] obtained for the concerned solid phases are used as criteria for determination of solids susceptible to precipitate under measured physico-chemical conditions. A saturation index of zero indicates equilibrium, a positive value indicates oversaturation and a negative value undersaturation.

Thermodynamic calculations show a permanent supersaturation ( $0.1 < p\text{CO}_2 < 1.0$  atm) of the studied waters with respect to the atmospheric  $p\text{CO}_2$  (3.2–4 atm). Amorphous silica [−0.09, 0.15] is saturated and will precipitate from the major part of the Cézallier and Ste Marguerite fluids. Barite [−0.03, 0.37] is also close to the equilibrium. The carbonate precipitations are certainly mixed minerals (Sr,Mn,Fe,...,Ca) $\text{CO}_3$ (s), according to the saturation states of the different carbonate minerals (aragonite [−0.344, 0.94], calcite [−0.20, 1.09], magnesite [−1.10, 0.50], siderite [−2.29, −0.42], strontianite [−0.12, 1.29], and witherite [1.19, 2.46]). The amorphous hydrous iron oxide,  $\text{Fe}(\text{OH})_3$ -am. [−3.48, −0.29], and gibbsite [1.42, 1.71], will also precipitate.

### Evidence for microbial mediation

SEM investigations were undertaken to determine the crystalline or amorphous morphology of both deposits. The carbonate deposit presents millimetre bands reflecting seasonal changes in the precipitation with obvious colours of vegetation and sometimes of iron content. Most samples are structured by

encrusted filaments corresponding to cyanobacteria remains. The morphology and orientation of the filaments are nicely preserved by the carbonate coating, whereas the sample surface is covered by diatom frustules. Such carbonate precipitation is commonly linked to bacterial activity and calcite crystals use bacteria bodies as nuclei [6].

Regular shaped crystals of calcite are indicating a rather slow growth without competition for space. Aggregates of small calcite crystals (1 $\mu\text{m}$  average size) are quite well represented in each sample; some are organised in volumes evocating biological spheres. The weak acid attack reveals grapes of bacterial colonies with an iron-enriched composition (Fig. 1). The oxide samples correspond to dense aggregates of smaller particles with evidences of iron-grapes as in the carbonate samples. At this state of observation it is not possible to conclude on which process mainly contributes to the oxide precipitation. However, the identification of similar grape colonies in the two deposits is in favour of organic influence. Bacteria could initiate, or at least positively influence, the oxide precipitation.

The microscopic features of both precipitations indicate microbial mediation as a probable part of the formation mechanism in the presence of iron bacterial colonies. The recognition of the role of bacteria in hot spring deposits is increasing even for oxide formations [1]. The Cézallier hydrothermal spring precipitations demonstrate yet again that the carbonate micro morphology, whether etched or not, presents microbe-like forms indicating former presence of life.