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# New Peak Temperature Constraints using RSCM Geothermometry on the Hajjar Zn-Pb-Cu Mine and its Surroundings (Guemassa Massif, Morocco)

Sylvain Delchini\*, Abdeltif Lahfid\*, Claire Ramboz, Yannick Branquet

\* BRGM, 3 avenue Claude Guillemin, 45060 Orléans, France - [s.delchini@brgm.fr](mailto:s.delchini@brgm.fr)

CNRS, ISTO, UMR 7327, 45071 Orléans, France

Université d'Orléans, ISTO, UMR 7327, 45071 Orléans, France

Lhou Maacha

MANAGEM, Groupe ONA, 52, av. Hassan-II, Casablanca, Maroc

**Abstract.** This study aims at precisizing the thermal history of the Guemassa massif and that of the Hajjar polymetallic deposit, by using a recently-developed method: the Raman Spectroscopy of Carbonaceous Material (e.g. Beyssac et al 2002; Lahfid et al 2010). The Guemassa massif belongs to the Moroccan Meseta domain and is mainly composed of Palaeozoic rocks folded during the Hercynian orogeny. This area underwent tectonic, metamorphic and hydrothermal events that explain the presence of several base metal deposits like Hajjar. The application of Raman Spectroscopy of Carbonaceous Material geothermometry (RSCM) has revealed new temperature peaks superior to 500°C that were unrevealed by other methods (fluid inclusion, chlorite thermometry). This new data set will allow a better understanding of the thermal history and of the mineralization processes in the Guemassa massif.

**Keywords.** Hercynian massif, Moroccan Meseta, base metal Hajjar deposit, SEDEX-VMS type, peak temperature, RSCM geothermometry, polythermal history.

## 1 Introduction

Understanding the thermal history of rocks is a key element for reconstructing the history of basins or mountain belts for mining industry. Many geothermometers are used to estimate paleotemperatures like mineralogy, isotopes, illite crystallinity. However, these methods cannot be applied in all metamorphic contexts. For instance, metamorphic rocks that contain appropriate mineral assemblages are relatively rare and mineral retro-morphism may affect peak temperature accuracy. An alternative approach is to use Carbonaceous Material (CM) that forms by metamorphic transformation of organic matter originally present in the rock. CM is a common compound of sedimentary and metamorphic rocks. The study of the maturity of CM provides a relatively precise tool to estimate the thermal evolution of rocks and therefore to provide relevant constraints on the burial/exhumation history of geological formations. Both the CM structure and chemistry give information about the degree of transformation during the geological history that involves carbonization during advanced diagenesis, low-grade metamorphism and graphitization under more intense metamorphism.

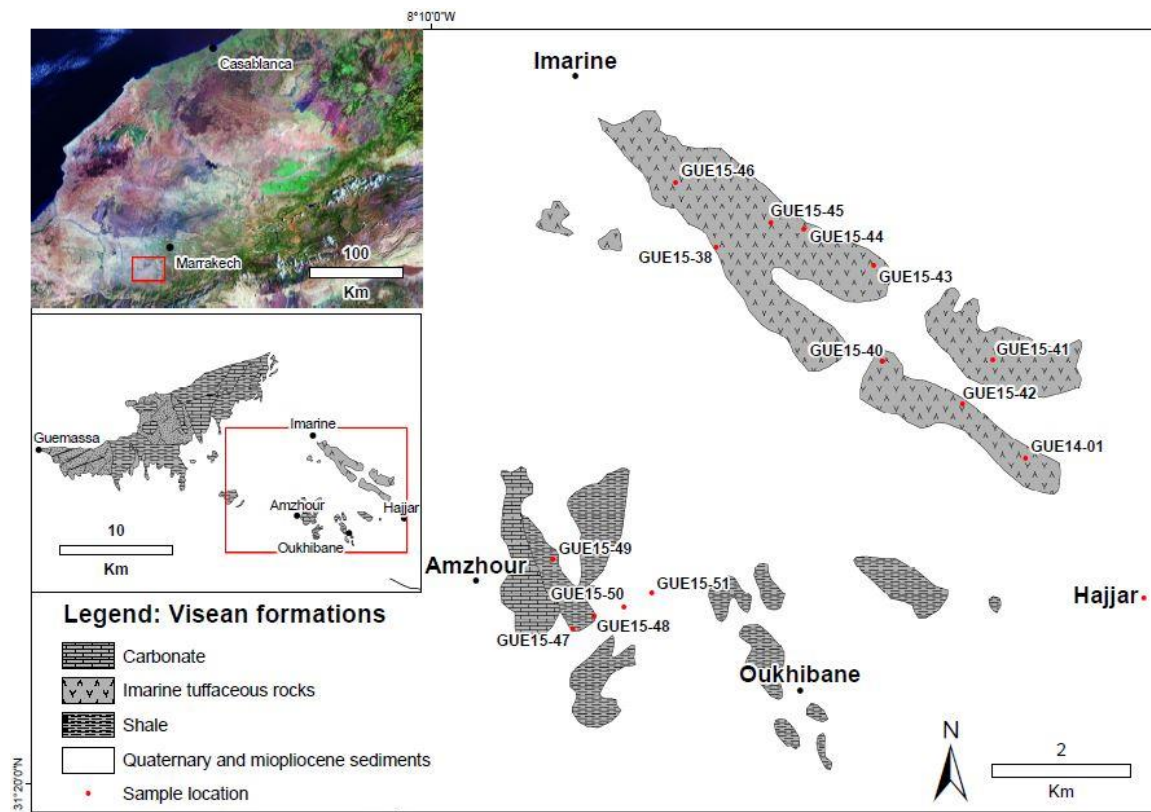
The characterization of the CM structure by Raman Spectroscopy can be used to estimate temperature maxima. Consequently, a new geothermometer has been developed, namely the Raman Spectroscopy of Carbonaceous Material (RSCM). This tool measures the structural evolution of the organic matter that is present in rocks. A version of the RSCM, designed to accurately measure temperatures ranging from 330° to 650°C, was first developed by Beyssac et al (2002). Its application range was later expanded to lower temperatures between 200° and 350°C by Lahfid et al (2010).

The objective of this study is to determine maximum paleotemperatures in the Hajjar polymetallic deposit and its surroundings, which correspond to the N'Fis domain in the eastern part of the Guemassa massif, Morocco.

Combining RSCM data with the ones of more classical thermometric methods like fluid inclusions and chlorite thermometry, will allow a good understanding of the Hajjar deposit complex thermal history.

## 2 Geological setting

The Guemassa massif (Fig. 1) belongs to the Moroccan Meseta, mainly constituted of Palaeozoic rocks folded during the Hercynian orogeny. During the Carboniferous, the massif experienced individualization of a subsidizing basin with coeval intense syn-sedimentary volcanic activity, associated with massive sulphide mineralization (dominated by pyrrhotite and exploited for Cu, Pb, Zn), like the Hajjar deposit. Such deposits show intermediate characteristics between SEDEX and VMS, like the massive sulphide of the Iberian Pyrite Belt (IPB). Based on the predominance of pyrrhotite, Hajjar was classified as a "Guemassa-Jebilet" sub-type distinct from the pyrite-dominant IPB type (Hibti 2001; Hibti and Marignac 2001). During the Upper Carboniferous (Westphalian), a major Hercynian deformation event was responsible for the development of an epizonal metamorphism. Several stratigraphic, structural and metamorphic studies were conducted in this massif (e.g. Hibti 1993 and references therein).



**Figure 1.** Structural map of the N'Fis domain with location of the studied samples (modified from Haimeur 1988).

## 2.1 Stratigraphy

The Guemassa massif is mainly composed of Visean sediments (Fig. 1). These sediments, associated with bimodal magmatism, form a volcano-sedimentary series (e.g. Haimeur 1988).

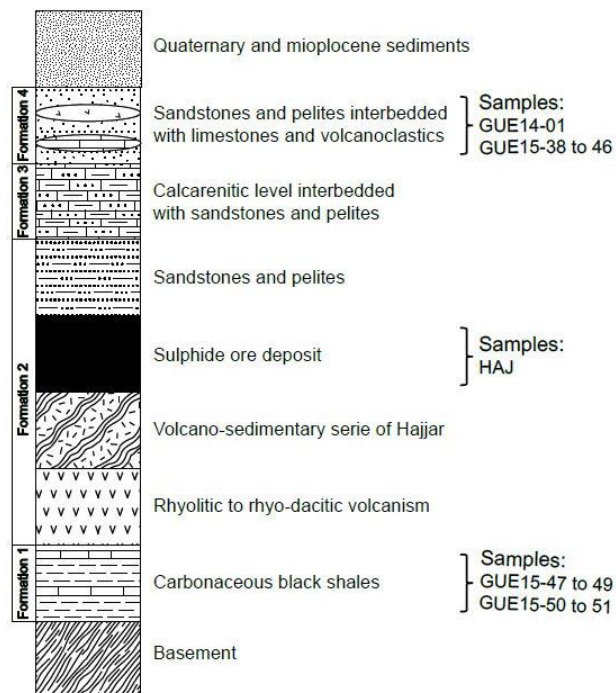
In this work, we particularly focused on the N'Fis domain (Fig. 1). Figure 2 presents the stratigraphy of the N'Fis domain, characterized by four main units from bottom to top (Hibti 1993, 2001): formation 1 (sector of Amzhour) is composed of carbonaceous black shales intercalated with sandstone beds at the top; (2) formation 2 (sector of Oukhibane and Hajjar) contains black shales and a sulphide ore body related to rhyolitic to rhyo-dacitic volcanism (volcano-sedimentary series of Hajjar). The mineralization is mainly composed of 50-75% pyrrhotite associated with other sulphides (sphalerite, galena, chalcopyrite, pyrite, arsenopyrite); (3) formation 3 is characterized by sandstones and pelites dominated by calcarenite beds (sector of Oukhibane and Hajjar); (4) the upper formation (sector of Imarine) shows a succession of sandstone beds and shales intercalated with volcanoclastics and overlain by carbonate sediments.

## 2.2 Deformation and metamorphism

Several tectonic phases occurred in the Guemassa massif. These phases can be correlated with tectonic events that affected the entire Meseta domain during the Palaeozoic. Three phases of deformation have been identified in the Guemassa massif and Hajjar deposit (e.g. Hibti 1993 and references therein).

- The syn-sedimentary phase (D0) occurred at the Visean-Namurian. This episode is responsible for the

development of syn-sedimentary structures, both in the mineralization and in its host-rock. Normal faulting and slumps reveal tectonic instabilities during sedimentation.



**Figure 2.** Detailed synthetic lithostratigraphic column of the N'Fis domain (Hibti 2001) and localization of the studied samples.

- The D1 phase corresponds to the beginning of the Hercynian phase characterized by the formation of folds and NW-SE-oriented schistosity (S1). This deformation is accompanied by regional greenschist facies

metamorphism characterized by a quartz-albite-chlorite-muscovite assemblage.

- The D2 phase is characterized by the development of folds and a NE-SW-oriented schistosity (S2) that interacted with S1, leading to the formation of a crenulation cleavage. This deformation is accompanied by low-grade metamorphism with sericite as the main mineral.

In the N'Fis domain, a late post-kinematic metamorphism responsible for the development of biotite, cummingtonite and anthophyllite has been described (Hibti 1993, 2001). This biotite yielded a  $^{40}\text{Ar}/^{39}\text{Ar}$  age of c. 301 Ma (Watanabe 2002). It is important to note that an andalusite - cordierite contact metamorphic assemblage has been locally observed in the Hajjar deposit (Hibti 1993).

These petrographic and chronological data suggest the presence of a deep plutonic intrusion below the N'Fis domain at the Upper Carboniferous.

### 3 Methodology

#### 3.1 RSCM geothermometry

The CM trapped in rocks is chemically and structurally modified, following to burial and gradual heating from advanced diagenetic to metamorphic conditions (Beysac et al 2002; Lahfid et al 2010).

Raman spectroscopy is one of the most suitable technique to analyse these CM transformations. The CM spectra are interpreted as a function of temperature using the calibration of Beysac et al (2002) and Lahfid et al (2010). It is important to note here that the RSCM method has been successfully applied in different geological contexts. Numerous studies thus confirmed that RSCM is a reliable tool to determine peak temperatures of rocks with an accuracy of  $\pm 25^\circ\text{C}$ .

Raman spectra were obtained using a Renishaw InVIA Reflex microspectrometer (BRGM-ISTO; Orléans). A laser (514 nm) was focused on the sample by a DM2500 Leica microscope equipped with an x100 objective (NA = 0.90).

The Raman spectrometer was operated using static scanning, in a window centered at  $1580\text{ cm}^{-1}$  which includes all the first-order bands and allows a properly definition of the baseline. Instrument control and Raman measurements were performed with the software package Renishaw Wire 4.0. Acquisition times (generally over 10 seconds) and accumulations of spectra vary between 5 and 10. In this study, all samples were analysed using thin sections exposed to a laser beam with power of 0.5 mW at sample surface. In order to check that the within-sample structural heterogeneity is limited, at least 10 spectra are recorded for each sample.

#### 3.2 Sampling Strategy

The samples used in this study were collected in the N'Fis domain (Figs. 1, 2). They come from outcrops around the Hajjar mine (14 samples noted GUE) and from different depths in the Hajjar body (10 samples noted HAJ collected in the footwall and hangingwall of the massive ore)

## 4 Results: Thermometric data

### 4.1 Previous thermometric works

Different geothermometric methods were applied to the N'Fis domain, including the Hajjar deposit, in order to understand their thermal history. These methods are essentially fluid inclusions, chlorite thermometry and mineralogy. Fluid inclusion data (Essarraj 1999) show temperatures around  $360^\circ\text{C}$  at a trapping pressure of 2.4 kbar. This temperature is in agreement with the low-grade, quartz-albite-chlorite-muscovite metamorphic D1 assemblage (e.g. Hibti 1993, 2001).

Other fluid inclusions, which exhibit homogenization temperatures of  $400^\circ\text{--}425^\circ\text{C}$ , are interpreted to represent maximum post-kinematic temperatures reached in the N'Fis domain (Essarraj 1999; Hibti 2001). During this late hot thermal event, the N'Fis domain experienced the pervasive development of static biotite and/or cummingtonite, anthophyllite porphyroblasts that overprinted previous deformation assemblages (Hibti 2001).

### 4.2 RSCM data

The Raman spectra of CM acquired in this study comprise three bands which are the G-band located at around  $1580\text{ cm}^{-1}$ , the D1-defect band located at around  $1350\text{ cm}^{-1}$  and the D2-defect band located at around  $1620\text{ cm}^{-1}$ . Obtained Raman spectra mainly differ in the relative area of their D1-band (Fig. 3).

Referring to quantitative calibration, the maximum temperatures obtained by the RSCM method show values of  $500^\circ \pm 25^\circ\text{C}$  in the N'Fis domain, except for the rocks in contact with the Hajjar body where temperatures reach  $550^\circ \pm 25^\circ\text{C}$  (Fig. 3).

## 5 Discussion and conclusion

Previous works have shown that three thermal events have affected the N'Fis domain, including the Hajjar deposit (Hibti 1993, 2001; Essarraj 1999).

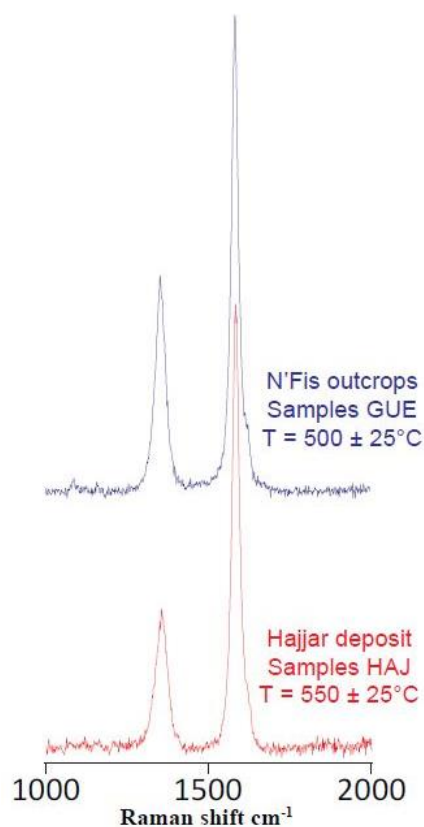
The first thermal event recorded in the N'Fis domain is generated by the syn-sedimentary bimodal magmatism, producing the circulation of sulfide-rich fluids with temperatures greater than  $250^\circ\text{C}$ . These temperatures were calculated with geothermometers on sphalerite and chlorite which preserved a primary chemical composition (Hibti 2001).

The Hercynian phase marks the second thermal episode having affected the N'Fis domain. This episode induced a regional greenschist facies metamorphism, as shown by mineralogy (chlorite-muscovite-quartz assemblage) and fluid inclusions (which indicated pressure-temperature conditions around 2.4 kbar and  $360^\circ\text{C}$ ).

The third thermal episode is described as post-Hercynian (Essarraj 1999; Hibti 2001), with a temperature of  $450^\circ\text{C}$  deduced from mineralogy and fluid inclusions.

Our peak temperature estimates show values superior to  $500^\circ\text{C}$ . These temperatures differ from the ones obtained by other classical methods, which are not higher than  $450^\circ\text{C}$ . Nevertheless, fluid inclusion homogenization

temperatures of 450°C represent minimum trapping temperature conditions, since the fluids were trapped above boiling conditions. Also, 450°C represents minimum thermal condition for the biotite isograd (Hibti 2001). Higher Raman temperatures obtained in this work confirm the hypothesis of a late heat flow related to a deep granitic intrusion (Hibti, 2001). This intrusion could be closer to the Hajjar deposit which would explain the higher Raman temperature around the mineralization.



**Figure 3.** Representative Raman spectra of carbonaceous material of GUE and HAJ samples analyzed in this study.

It is important to properly evaluate the consequences of this high late heat flux on the Hajjar mineralization, as it may have caused the recrystallization of the ore, with an increase of the particle size related (Hibti, 2001). This thermal event could also have generated new mineralizing fluids (Marshall et al 2000; Vokes 2000).

That is why future work will include the acquisition of complementary geochemical, chronological and structural data to better explain these high temperatures and to

analyze their impact on the mineralization and their possible link with different mineralization processes.

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