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Mineralogical and petrophysical analysis of the GEo-01 and GEo-02 cuttings

Report n.	GEG2021008
Date	22.10.2018
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heatstore
High Temperature Underground
Thermal Energy Storage

Table of contents

1. SUMMARY

In the framework of the GEOTHERMICA ERA-NET co-funded project-HEASTORE, one of the main challenges related to assessing the technical feasibility and sustainability of High Temperature (~25°C to ~90°C) Aquifer Thermal Energy Storage (HTATES) is characterization of the mineralogical composition of the reservoir rocks which control the water rock interactions that can activate in response to the cyclic production/injection of hot water. These reactions have an impact on the potential of dissolution and precipitations of mineralogic phases in the reservoirs and corrosion and scaling potential at borehole and surface equipment scales. In this report we present detailed description of the results from the laboratory analysis carried out on the cuttings material collected from the GEo-01 and GEo-02 geothermal exploration borehole sites situated in the Geneva Basin, Canton of Geneva.
The collection of the cutting samples has been carried out in collaboration with Services Industriels de Geneve and HydroGeo Environnement during drilling operations as part of **Task 3.1 On site Mineralogical and petrophycal analysis, Interpretation of logs** of the proposal submitted to BFE and ***Task 4.1: Case study feasibility assessment and technical design for Demonstration*** of the European proposal. Analysis and interpretations were carried out in the framework of ***Task 1.1 Specification and characterization for ATES concepts*** of the proposal submitted to BFE in support the geochemical study performed by UniBe in WP2 of the Swiss proposal.

The Automated Quantitative Evaluation of Minerals by SCANning electron microscopy (QEMSCAN) analysis was used to provide a rapid and accurate evaluation of mineral phases in materials. QEMSCAN analysis were performed using a FEI QEMSCAN® Quanta 650F facility installed at the Department of Earth Sciences at University of Geneva. In Addition, Inductively Coupled Plasma Mass Spectrometry or ICP-MS was used for elemental determinations. The whole-rock compositional data for ten major elements and thirty-seven trace elements was acquired by ICP-MS with the same cuttings used for QEMSCAN analysis. The ICP-MS data acquisition was performed at Bureau Veritas laboratory (Vancouver, Canada).

The petrological and geochemical study of the GEo-01 and GEo-02 wells samples revealed important information about the main sedimentary formations of the Upper Jurassic and Lower Cretaceous.
This study demonstrates the importance of mineral analysis and whole rock geochemistry as effective tools to support subsurface exploration in poorly known sedimentary basins. The use of high resolution petrographic analyzes provided by QEMSCAN allowed the recognition and description of the main stratigraphic units of the Mesozoic sedimentary sequence.
By using QEMSCAN and ICP-MS, the present work was able to analyze a large number of thin sections, recognizing and characterizing the main formations crossed by the GEo-01 and GEo-02 exploration wells, defining chemo-zones and chemo-units that can be correlated in the Mesozoic of any future exploration/production wells. Moreover, these zones can be implemented in 3D subsurface models, geological models and geochemical models in order to better define the lateral facies variations, chemical changes and predict reservoir volumetrics along the basin.

2. INTRODUCTION

Important lateral variations of facies and reservoir properties have been observed in the Geneva Basin (Clerc et al., 2015; Makhloufi et al., 2018; Moscariello, 2016; Rusillon, 2018; Moscariello et al., 2020). In the context of the geothermal development of the Canton of Geneva, these variations represent a challenge to better understand, asses and predict the reservoir properties and locate suitable targets for geothermal production. The GEothermie 2020 exploration program led by the Services Industriels de Genève (SIG) led to the drilling of two medium-depth exploration wells (GEo-01 and GEo-02). Within the purpose of exploring, identifying and characterizing the geological and hydrogeological of the Mesozoic units in the basin, these two new wells produced new data critical to better understand the lateral variations of sedimentological facies in the basin.

In order to asses these variations, a complete petrographic, mineralogical and geochemical characterization of whole-rock (cuttings) samples issued from these wells was performed. This characterization was performed using QEMSCAN and ICP-MS analysis at high vertical resolution.

GEo-01 is the first medium-depth exploration well. It reached a depth of 745 m drilling through 407 meters of Oligocene Molasse, 241 meters of Lower Cretaceous limestones and reached the Upper Jurassic (Tithonian) limestones at a final depth of 745 meters below ground floor. GEo-02 well is 1456 m deep and drilled through 767 m of Oligocene Molasse, 229 m of Lower Cretaceous limestones and 446 m of Upper Jurassic limestones (Figure 1).

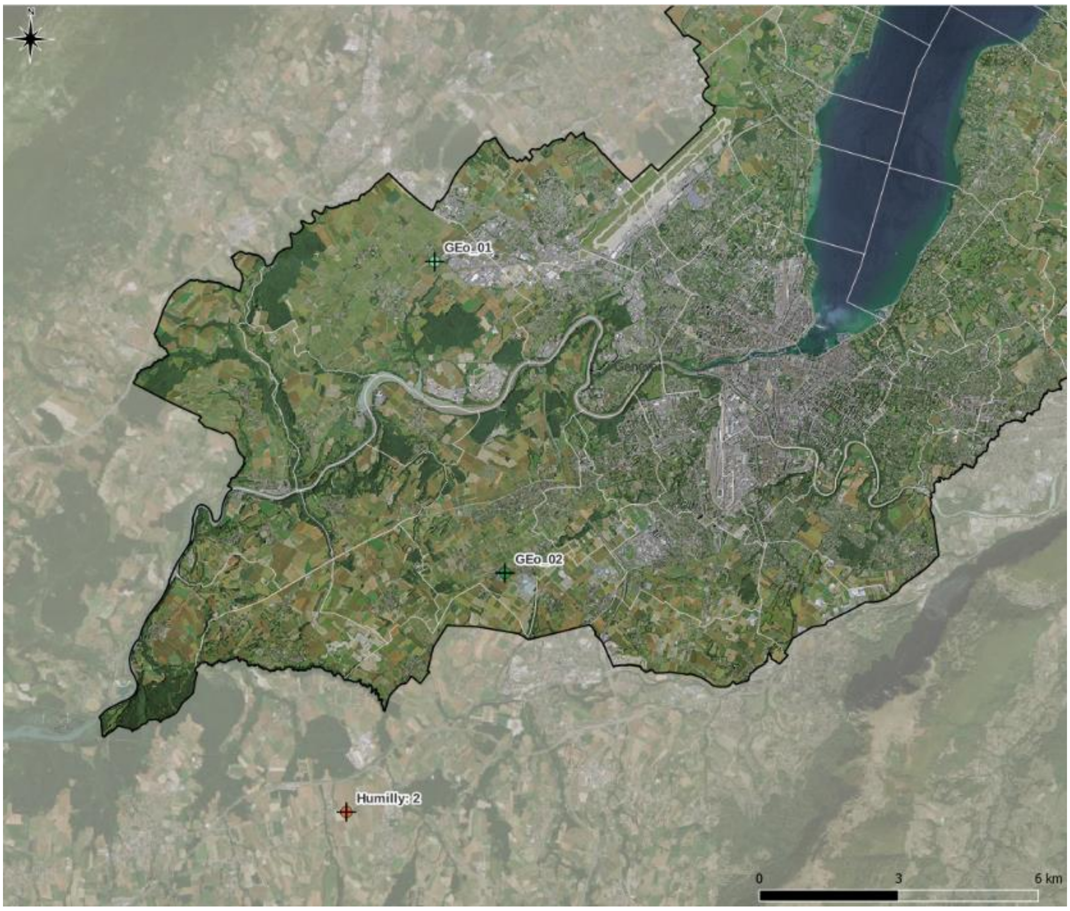

Figure 1 – Localization of the GEo-01, GEo-02 and Humilly-2 wells

3. METHODOLOGY

The Automated Quantitative Evaluation of Minerals by SCANning electron microscopy (QEMSCAN) analysis provides a rapid and accurate evaluation of mineral phases in materials, and presents it as a 2D map of their distribution through the sample (2D view only). QEMSCAN analysis were performed using a FEI QEMSCAN® Quanta 650F facility installed at the Department of Earth Sciences (University of Geneva, Switzerland) Sample preparation method (adapted from Zanoni et al., 2016) included washing of ditch cuttings have been which were then hand-picked to remove remnants of drilling mud before thin section preparation. QEMSCAN analyses were performed with a 15kV acceleration voltage and a probe current of 10 nA. The X-ray acquisition was 10’000 counts per pixel using a point-spacing grid of 10µm. The scanned thin section surface was around 14x20 mm where the mineral phase identification was made thanks to the combination of back-scattered electron (BSE) contrast and EDS spectra giving information on the elemental composition (Gottlieb et al., 2000). A mineral name was then assigned to each acquisition point by comparing its X-ray EDS spectra to a library of known spectra initially provided by the manufacturer and improved in-house using a variety of natural standards. QEMSCAN® data processing was performed using the FEI iDiscover software. Then, for each sample, the QEMSCAN software provides a mineralogic maps.

Inductively Coupled Plasma Mass Spectrometry or ICP-MS is an analytical technique used for elemental determinations. This technique consists on the atomization of the samples creating atomic and small polyatomic ions, which are then detected (Jarvis, 1988). It is known and used for its ability to detect metals and several non-metals in liquid or solid samples at very low concentrations. It can detect even different isotopes of the same element, which makes it a versatile tool in isotopic studies. Geochemical analysis labs were early adopters of ICP-MS technology because of its superior detection capabilities, particularly for the rare-earth elements (REEs). The ICP-MS allows determination of elements with atomic mass ranges 7 to 250 (Li to U), and sometimes higher (Jenner et al., 1990). Sensitivity of the instrument is typically around 1 million cps (counts per second) for a 1 ng/g solution of the element indium (mass 115In) and the detection limits of many elements are in the pg/g to fg/g range (Lichte, 1988). The whole-rock compositional data for ten major elements and thirty-seven trace elements (including REEs) was acquired by ICP-MS with the same cuttings used for QEMSCAN analysis. The ICP-MS data acquisition was performed at Bureau Veritas laboratory (Vancouver, Canada).
A summary of the number of samples and coverage of the analysis is summarized in Table 1.

Table 1 – Summary of analysed samples

Well	Analysis	Number of samples	Coverage
GEo-01	QEMSCAN & ICP-MS	87	Upper Jurassic – Oligocene
GEo-02		133	

Table 1 – Summary of analyses performed on well cuttings

Due to the COVID pandemic, the analyses of GEo-02 samples are incomplete. QEMSCAN data are available from the top-Lower Cretaceous to the top-Oligocene only. Analysis of the Cretaceous and Upper Jurassic is sill ongoing. Geochemical characterization and correlation were assessed using ICP-MS data. The initial stratigraphic sequence originates for mud-logging characterization acquired during drilling.

3.1. Mesozoic mineralogy and geochemistry in GEo-01

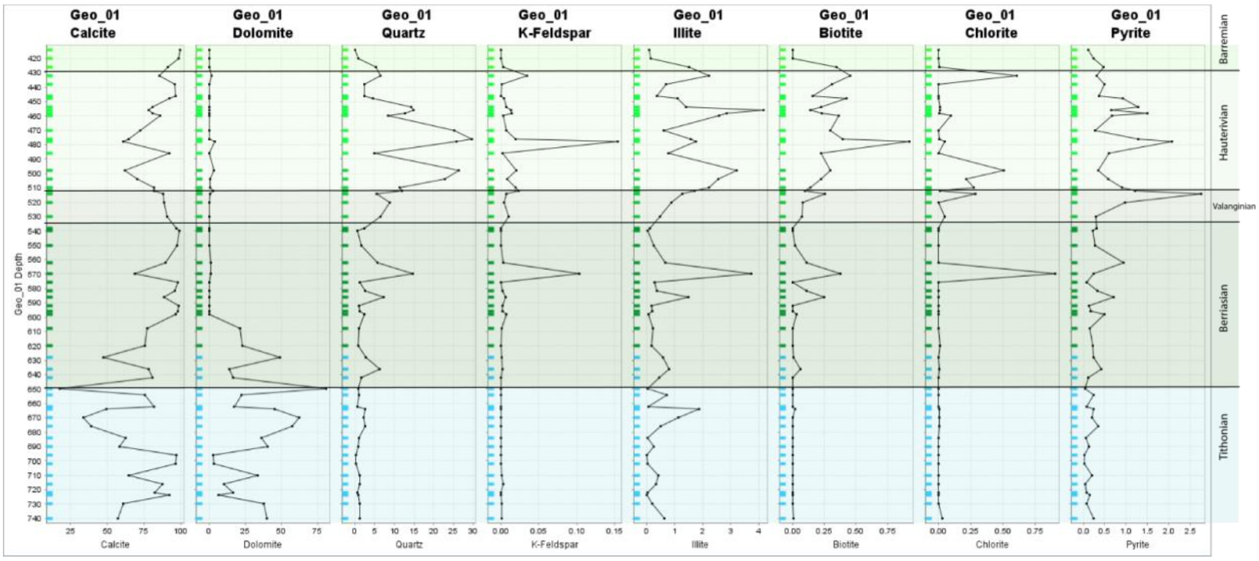

Figure 2 – Main mineralogy of GEo-01 from QEMSCAN. Stratigraphy is derived from the lithology report produced by Hydro-Géo Environnement.

3.1.1. QEMSCAN mineralogy

The mineralogy of GEo-01 obtained for QEMSCAN analysis divides the Mesozoic sedimentary sequence in two main packages (Figure 2). The first package extends from 740 to 598 m, covering the Tithonian. This package exhibits sediments rich in calcite, dolomite and some occurrences of quartz and illite. Dolomite can make about 25 to 30% of the mineralogy and at least one sub-unit exhibiting dolomite content >50% can be identified (680 to 665 m). Quartz shows small variations with a slight increase from 740 to 668 m, never reaching more than 3% and a spike at 645 m with almost 7%. Illite content is globally <2% but presents important variations. The Tithonian – Berriasian transition is marked by an important shift in calcite and dolomite content at 650m where calcite content drops to 17% while dolomite content increases up to 81%

The second package corresponds to the Lower Cretaceous and extends from 650m to 414m deep. Rocks are mainly composed of calcite and unlike the first package, dolomite is almost absent. On average calcite corresponds to 86.8% of the mineral composition of the analyzed sediments. In this package quartz is more abundant and reaches in average 8.8% of the mineralogical composition of this package. A first remarkable transition is observed at 570m deep, in the middle-Berriasian, where calcite content drops from 98% to 68% while Quartz, K-Feldspar, Illite, Biotite and Chlorite all presents increased values. The Valanginian is then characterized by decreasing content in calcite while quartz, clays and tectosilicates content increases.

A second transition is observed at 498m, just after the Valanginian - Hauterivian transition (512 m) where Calcite content drops again to 61% while Quartz and other detrital minerals peaks. The same trends in compositions are again observed at 478 m and at a lesser degree at 456 m. At 478 m deep, Glauconite content also show the highest value observed in GEo-01 at 2.7%. The Hauterivian exhibits increasing content in calcite while quartz, tectosilicates and clay minerals content present important variations. The Hauterivian – Barremian transition is marked by a third remarkable transition at 432 m deep with similar trends of decreasing calcite content and increasing detrital content associated with a higher Glauconite content (1.05%).

The results of the QEMSCAN analysis revealed a sedimentary sequence composed mainly of calcite-rich carbonate rocks intercalated with marl rich deposits composed mainly of quartz, illite, pyrite, glauconite and apatite. Moreover, dolomite is predominant only in the Upper Jurassic while almost nonexistent in the Lower Cretaceous. Therefore, the relationship between the concentration of these minerals in the samples can be used to characterize each formation. Overall, calcite (79.2% mean) and quartz (5.9% mean) together make up 85.1% of the samples analyzed, so these two minerals were correlated using cross plots that provided a graphical view for each formation and facies identified (Figure 3).

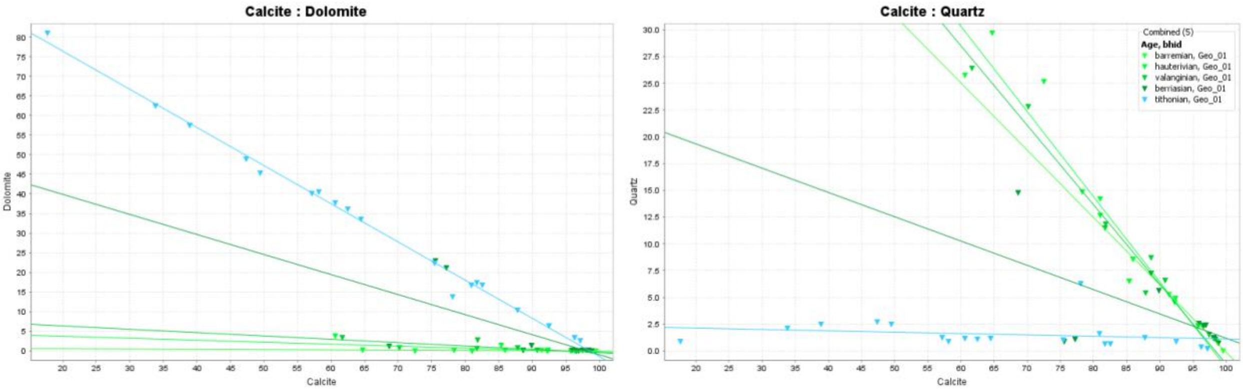

Figure 3. Cross-plots generated from calcite, dolomite and quartz concentrations in QUEMSCAN-analyzed samples in GEo-01. The Upper Jurassic and Lower Cretaceous limestones are easily discriminated by comparing the composition of these three minerals.

Throughout the GEo-01 well, the mineralogical content provided by QEMSCAN allowed the recognition of nine sedimentary formation and their respective facies (Figure 4). From bottom to top: Twannbach Fm. in the Upper Jurassic period, Goldberg Fm., Pierre-Châtel Fm., Vions Fm., Chambotte Fm., Vuache Fm., Grand Essert Fm., Gorges de l'Orbe Fm. (Jaune Urgonian) and Vallorbe Fm. (Blanc Urgonian).

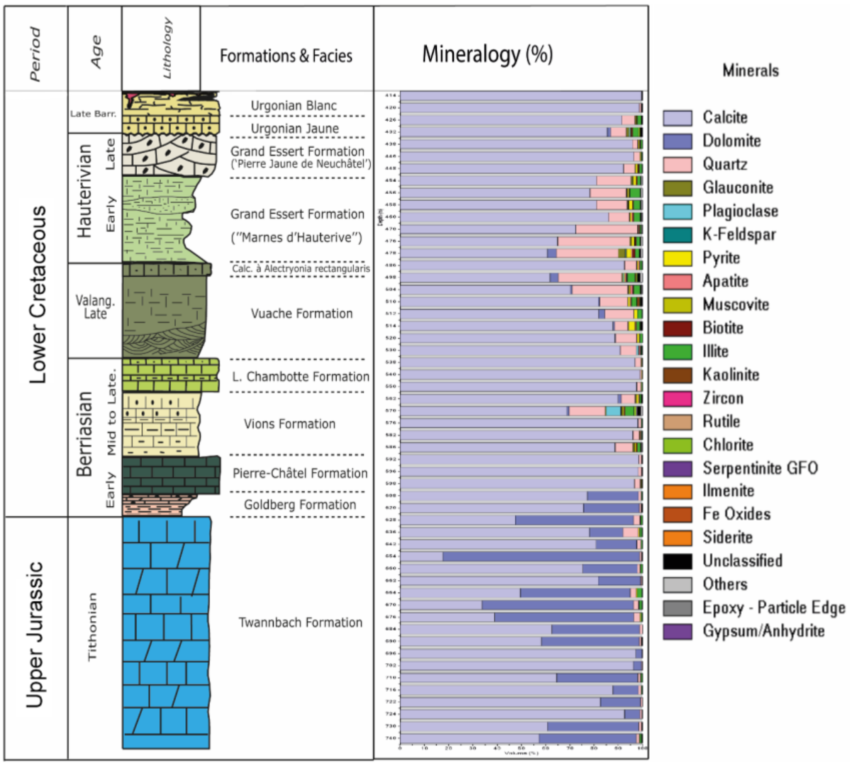

Figure 4. Litho-stratigraphic column proposed by the interpretation of the QEMSCAN analysis results. In addition, all sedimentary formations identified in the present study are listed and correlated with the results obtained.

3.1.2. Major, minor and rare earth elements

The major elements represent the main elemental composition of the sedimentary rocks analyzed in the present study. Coherently with QEMSCAN analysis, calcium (Ca) represents the major composition of the samples, with an average concentration of 33.4%. Throughout the vertical profile, the concentration of Ca varies widely but never reaches values below 23%. The richest intervals in Ca range from 540m to 650m (Figure 5). Another important element is magnesium (Mg). This element has an average concentration of 1.43% along the analyzed interval. Despite this low average, Mg values can reach up to 7.59% (654m). Two very distinct intervals can be observed: (1) from 740 m to 608 m with an average of 3.18% of Mg and (2) from 598 m to 414 m the concentration of this element is reduced to an almost constant average of 0.32%. These intervals are coherent with the presence of Dolomite (CaMg(CO3)2) put in evidence by the QEMSCAN analysis.

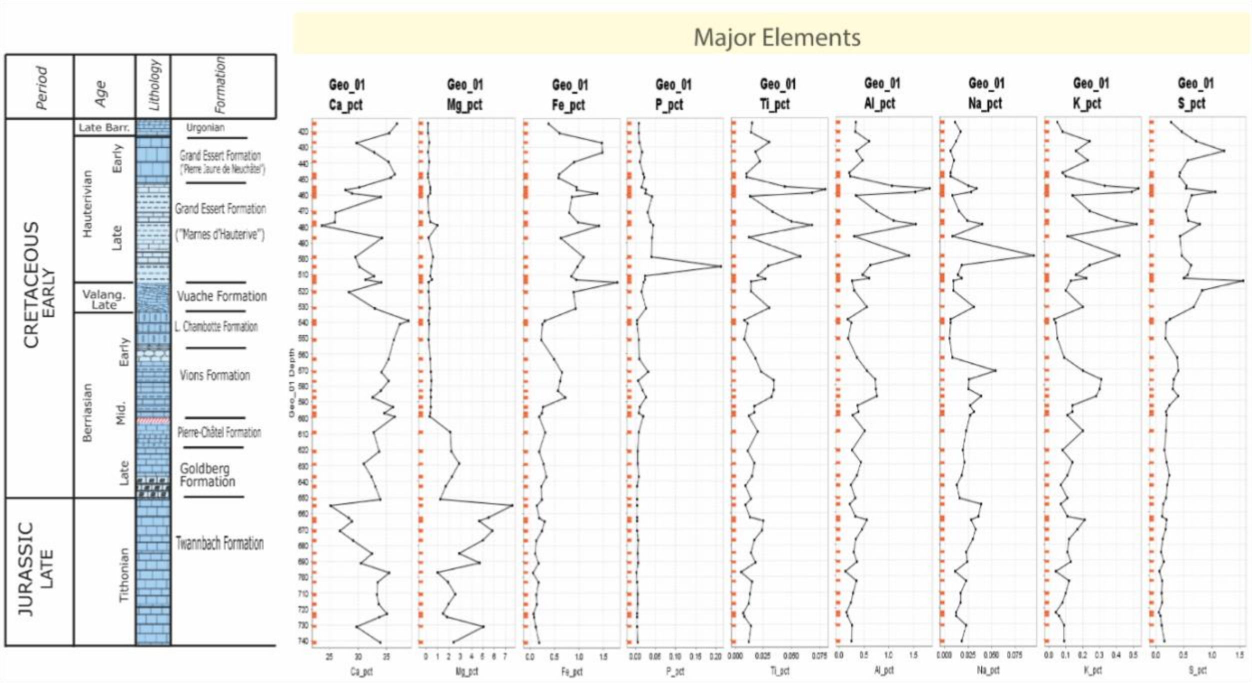

Figure 5 - Downhole elemental profiles obtained after processing of the ICP-MS results. The upper image shows the GEo-o1 lithostratigraphic column modified from the Litholog Report (LLR) provided by Hydro-Géo Environnement. To the right, the vertical concentration (ppm) profiles of some major elements for the present study are shown.

Broadly, along the vertical profile, the iron (Fe) content has an average of 0.55%. However, considering the variance trend of this element, three distinct intervals can be found (Figure 5). The first, from 740m to 590m is characterized by low and constant values that reach a maximum of 0.33%. From 596m, we notice an enrichment in Fe in the analyzed sediments reaching up to 0.72%. Advancing upwards in stratigraphy, from 538m, the presence of Fe in the sediments increases. To the top of the Mesozoic sequence, an average concentration of 0.97% Fe is noted, but these values vary greatly in this range, presenting iron "rich" intervals at the top of the studied interval.

Phosphorus (P) is generally very low or almost absent. This element constitutes on average 0.018% of the composition of the sampled sediments. However, a slight upward enrichment of P is seen from

600m. At a depth of 540m a large spike marks the richest level of P, which contains 0.212% of this element. From this level, P content returns to normal trend assuming lower values that gradually decrease upwards (Figure 5). The sulphur (S) content in the studied sediments is similar to that of Fe. In the lower part of the vertical concentration profile of this element (740m to 540m), lower values with average of 0.18% revel sediments with little or almost no content of S. However, the top of the sedimentary sequence (from 538m) exhibits sediments richer in S (average of 0.64%). Following the same behavior of the concentration trend of Fe, this element tends to concentrate at specific levels such as 514m, 458m and 432m, constituting up to 1.56% of the elemental composition of the sediments (Figure 5).

The other major elements titan (Ti), aluminum (Al), sodium (Na), and potassium (K), although having distinct concentration values, tend to concentrate on the same specific sedimentary intervals as S. Their concentrations are rather stable at low values in the Upper Jurassic, up until the middle Berriasian. However, towards the top of the studied sequence, five distinct depths, 570m, 498m, 478m, 476m and 456m present higher concentrations of these elements.

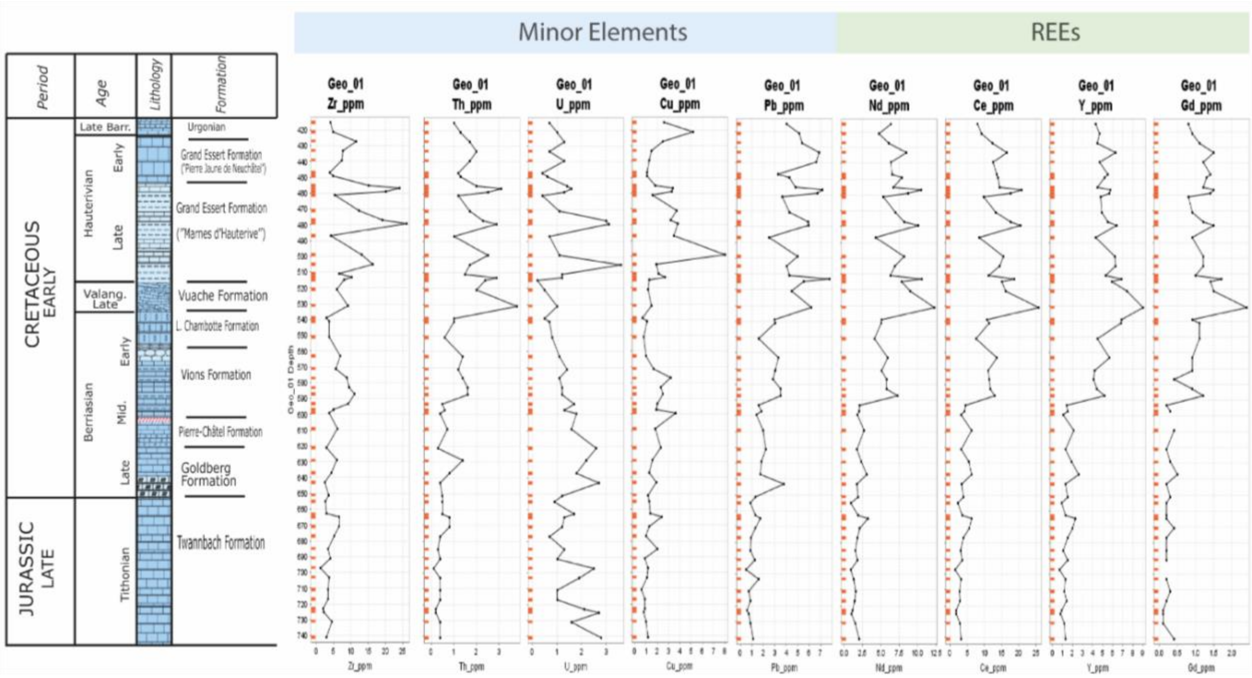

Figure 6 - Downhole elemental profiles obtained after processing of the ICP-MS results. The upper image shows the GEo-o1 lithostratigraphic column modified from the Litholog Report (LLR) provided by Hydro-Géo Environnement. To the right, the vertical concentration (ppm) profiles of some minor elements and REEs for the present study are shown.

The minor elements and the REEs (Figure 6) generally present lower concentrations in the sediments of the lower part of the analyzed sequence (up to 550m). Nevertheless, in the upper part of the Mesozoic sequence from 548 meters deep, the sediments tend to show higher concentrations of these elements in their composition. Both minor and REEs present the same general trends and spikes towards the top of the sequence with only copper (Cu) varying differently from the other. Positive spikes in the concentration trends of the minor elements and REEs (eg. 530m, 504m, 480m, 456m) indicate intervals where these elements are more abundant.

Using the results of ICP-MS analysis, a chemostratigraphic study of the Mesozoic sediments crossed by the GEo-01 well was conducted. This approach has been employed in carbonate reservoirs by several authors (e.g., Jorgensen, 1986; Ratcliffe et al., 2007; Davies et al., 2013, Craigie, 2015; Vishnevskaya et al., 2015; Eltom et al., 2017) looking at the quantity of clastic material in the analyzed samples and also the presence and distribution of immobile elements and REEs. By comparing elemental data with those of petrography, it is possible to establish the mineralogical affinities of the most abundant elements and minerals in the analyzed samples. The chemo zones were defined by variations in the content of major elements that represent most of the sediment's composition such as Ca and Mg. At these intervals the major elements have similar values on average and variation trends. After defined, each chemo zone was analyzed separately using the minor element variation and REEs being subdivided into chemo units (Figure 7).

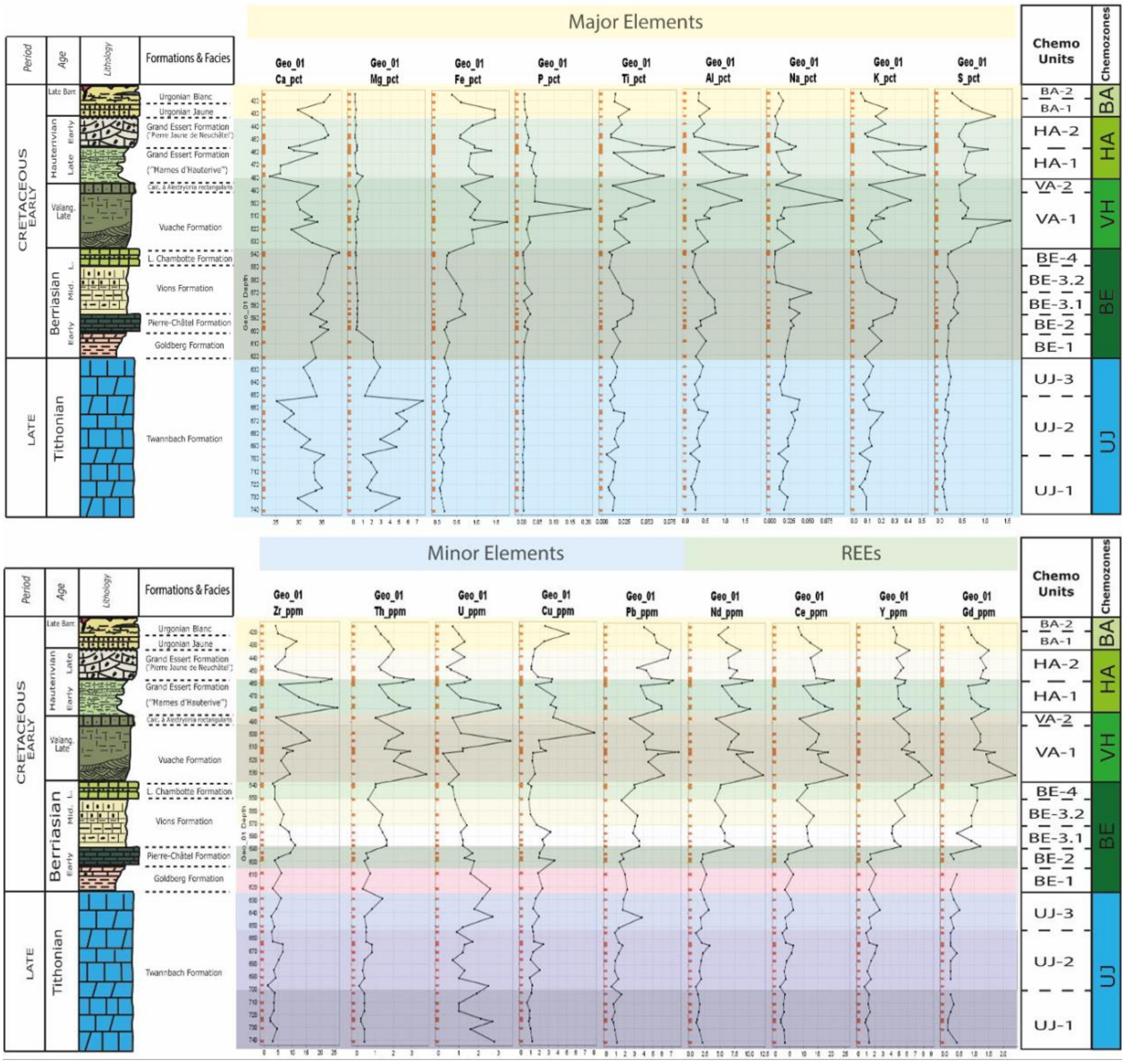

Figure 7 - Diagrams showing the interpretation of the results obtained by the ICP-MS analyses. The stratigraphic column was proposed by the present work and correlated with the vertical variation of the major elements, minor elements and REEs, used for the definition of the chemostratigraphic units.

3.2. Mesozoic mineralogy and geochemistry in GEo-02

Due to the COVID19 pandemic, QEMSCAN data are still not available for GEo-02. However, a high-resolution ICP-MS analysis of the Mesozoic sediments has been performed. Comparing GEo-02 results with GEo-01, major elements such as Ca, Mg, P, Na and S present significant differences. However, similar trends to what observed in GEo-01 are recognized in GEo-02 (Figure 8). Specific elements such as Ca, Fe and Al (Figure 8-A, B and C) present a heterogeneous repartition in the stratigraphy and present a clear distinction between the Upper Jurassic sediments (Kimmeridgian and Tithonian) and the Lower Cretaceous (Valanginian and Hauterivian). The Berriasian presents composition similar to the Upper Jurassic but its distinction is made by comparing cross-plots analysis of the elements (Figure 8-D and E).

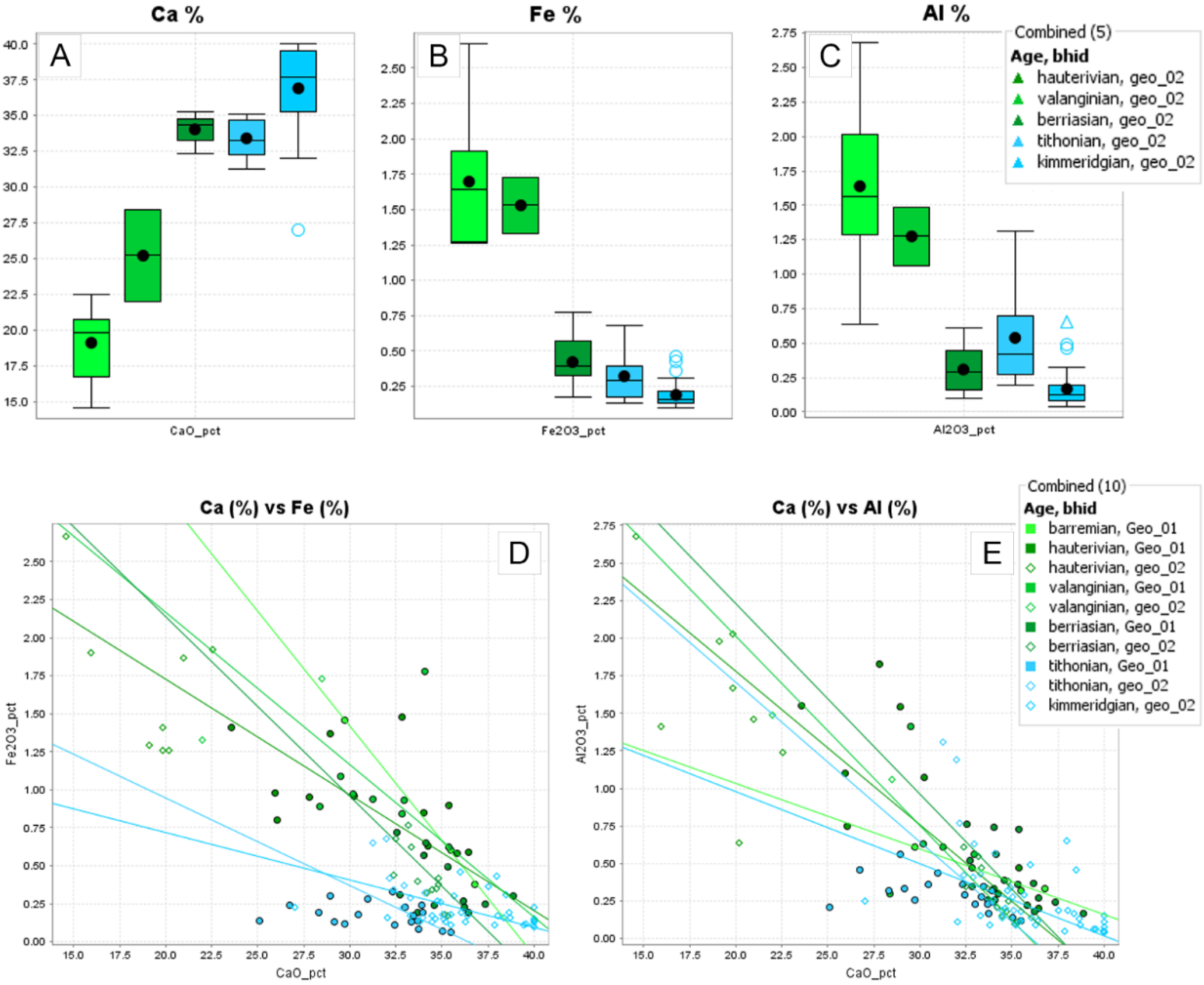

Figure 8 – Cross-plots of major elements in GEo-01 (blue squares) and GEo-02 (orange boxes).

As in GEo-01, Ca represents the major element of the samples, with an average concentration of 33.2%. Throughout the vertical profile, the concentration of Ca varies widely and reach values as low as 14% towards the top of the sequence. The richest intervals in Ca range from 1330 to 882m (Figure 9). The average concentration of Mg is 0.5% along the analyzed interval. Despite this low average, Mg values can reach up to 6.43% as a single spike of high Mg content (1390m). Unlike in GEo-01, no intervals can be easily defined by Mg alone and the rather constant low values could indicate that dolomite is less prevalent in GEo-02 than in GEo-01. Fe content has an average of 0.45%, almost as low as in GEo-01. However, as in GEo-01, three distinct intervals can be found (Figure 9). The first, from 1450m to 1030m is characterized by low and constant values that reach a maximum of 0.37%. From 1030m to 882m, we notice an enrichment in Fe in the analyzed sediments reaching up to 0.77%. Advancing upwards in stratigraphy, from 882m, the presence of Fe in the sediments increases. To the top of the Mesozoic sequence, an average concentration of 1.47% Fe is observed, with similar iron "rich" intervals as described previously in GEo-01. Phosphorus (P) is generally very low or almost absent. This element constitutes on average 0.018% of the composition of the sampled sediments, as in GEo-01. The same upward enrichment of P is seen starting at 882m and large spikes characterize the top of the sequence. Sulphur (S) variations mimics Fe variations, as in GEo-01. In the lower part of the vertical concentration profile of this element (1450m to 1200m), lower values indicate sediments with little or almost no content of S. However, the top of the sedimentary sequence (from 944m) exhibits sediments richer in S. As observed in GEo-01, S tends to concentrate on specific levels revealing sulfur rich intervals. In a similar way as what previously described for GEo-01, the other major elements Ti, Al, Na and K tend to concentrate on the same specific sedimentary intervals as S.

As the global variations and trends in GEo-02 chemical composition exhibits important similarity with GEo-01, chemo-zones and chemo-units defined in GEo-01 were then applied to GEo-02 to better define the stratigraphy (Figure 9).

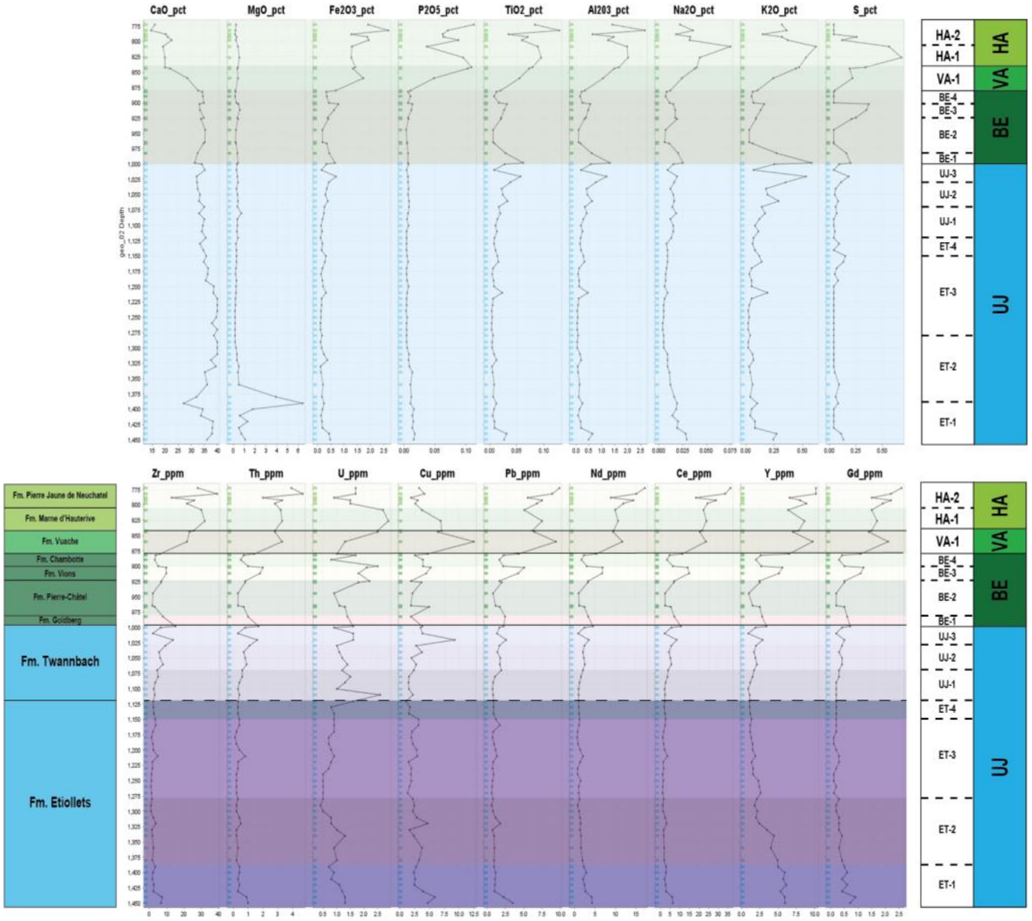

Figure 9 – Downhole plots of the interpretated ICP-MS analyses in GEo-02. The stratigraphic column was proposed by the present work and correlated with the vertical variation of the major elements, minor elements and REEs, used for the definition of the

chemostratigraphic units.

Four new chemo-units in the Upper Jurassic were defined specifically for GEo-02 as the well reached lower formation compared to GEo-01. Those new chemo-units separates the Etiollets formations into four distinct zones.

Using the chemo-units defined in this work, the chemostratigraphic correlation between GEo-01 and GEo-02 provided critical information on the lateral variations of thickness (Figure 10). Those variations are especially important in the Lower Cretaceous. Thickness in the Upper Jurassic seems to remain constant. However, as the complete stratigraphy of the Tithonian was not drilled in GEo-01, this assumption remains to be validated. In the Lower Cretaceous, the Goldberg Fm. exhibits the same thickness in the two wells. The Pierre-Châtel Fm. is significantly thicker in GEo-02 while both Vions Fm. And Chambotte Fm. are thinner. The Vuache, Marne d'Hauterive and Pierre-Jaune de Neuchatel Fm. are also thicker in GEo-02 than what observed in GEo-01.

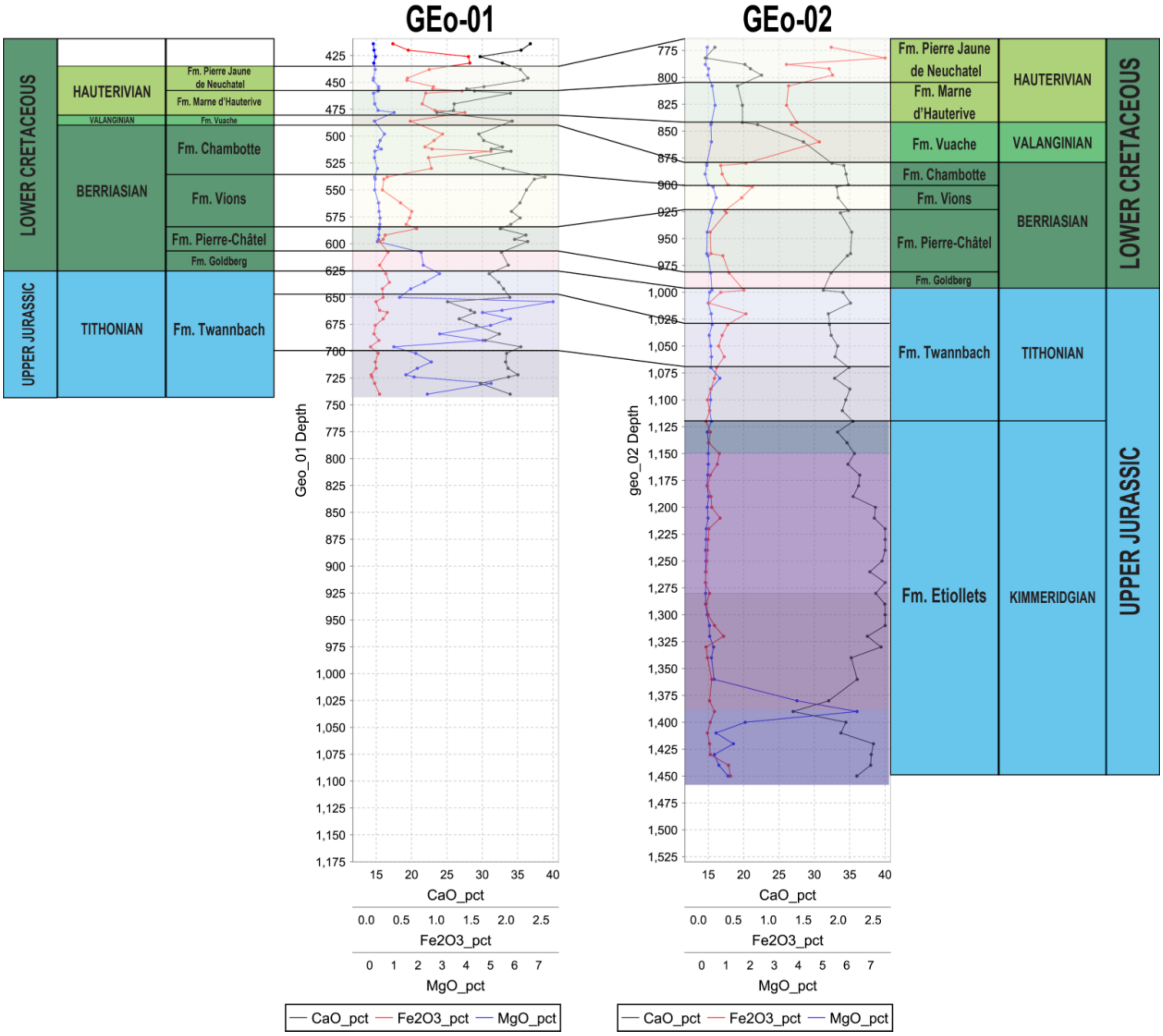

Figure 10 – Chemostratigraphic correlation of GEo-01 and GEo-02

4. CONCLUSIONS

The petrological and geochemical study of the GEo-01 and GEo-02 wells samples revealed important information about the main sedimentary formations of the Upper Jurassic and Lower Cretaceous. The comparison of these data with recent studies allows a better understanding of the Geneva Basin substrate and consequently the location of potential reservoirs. In outcrops, karsts were recognized in the uppermost Cretaceous units affecting principally the massive Urgonian limestones but are observed to extend at least down to the Pierre-Châtel Fm. (Signer and Gorin, 1995, Charollais et al., 2013; Mastrangelo et al., 2013; Godet et al., 2016). The lateral variations of thickness put in evidence by the chemostratigraphic correlations could have an impact on the quality and volumetric of reservoirs that are targeted for geothermal energy production in the Geneva Basin.

This study demonstrates the importance of mineral analysis and whole rock geochemistry as effective tools to support subsurface exploration in poorly known sedimentary basins. The use of high resolution petrographic analyzes provided by QEMSCAN allowed the recognition and description of the main stratigraphic units of the Mesozoic sedimentary sequence crossed by the GEo-01 well. The mineralogical and chemical variations observed along the upper Jurassic and lower Cretaceous sedimentary sequences enable the effective application of a chemostratigraphic approach. Usually, time-consuming petrographic and biostratigraphic studies are used to recognize the main sedimentary facies composing this type of deposits. However, by using QEMSCAN and ICP-MS, the present work was able to analyze a large number of thin sections, recognizing and characterizing the main formations crossed by the GEo-01 and GEo-02 exploration wells, defining chemo-zones and chemo-units that can be correlated in the Mesozoic of any future exploration/production wells. Moreover, these zones can be implemented in 3D subsurface models, geological models and geochemical models in order to better define the lateral facies variations, chemical changes and predict reservoir volumetrics along the basin.

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