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To cite this version:
M. Turpin, Fati H. Nader, Eric Kohler. Empirical Calibration for Dolomite Stoichiometry Calculation: Application on Triassic Muschelkalk- Lettenkohle Carbonates (French Jura). Oil & Gas Science and Technology - Revue d’IFP Energies nouvelles, 2012, 67 (1), pp.77-95. 10.2516/ogst/2011173. hal-00702884

HAL Id: hal-00702884
https://ifp.hal.science/hal-00702884
Submitted on 31 May 2012

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Empirical Calibration for Dolomite Stoichiometry Calculation: Application on Triassic Muschelkalk-Lettenkohle Carbonates (French Jura)

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Résumé — Calibration empirique pour le calcul de la stœchiométrie de la dolomite : application aux carbonates triassiques du Muschelkalk-Lettenkohle (Jura français) — Cette étude propose une approche pour la quantification de la dolomite et le calcul de sa stœchiométrie grâce à l'utilisation de la diffraction des rayons X couplée aux affinements de maille et de Rietveld et complétée par de nombreuses données issues de la littérature. Elle permet d'obtenir une meilleure justesse et précision pour la quantification de la dolomite (et des autres phases minérales) ainsi que pour le calcul de sa stœchiométrie par rapport à l'équation de Lumsden et de méthodes antérieures. L’approche proposée est vérifiée grâce à l’analyse d’un échantillon référence de dolomite (Eugui) et appliquée à des roches carbonatées du Trias (Muschelkalk supérieur-Lettenkohle) du Jura français. Elle est combinée à une étude pétrographique et isotopique et peut être appliquée tant aux roches qu’aux ciments dolomitiques.

Les dolomies du Muschelkalk supérieur se sont formées au cours d’une dolomitisation d’enfouissement associée à des fluides dont la température augmente et ayant une composition isotopique variable au cours de l’enfouissement. Outre la pétrographie, ceci est également mis en évidence par le pourcentage de Ca calculé dans les dolomites, qui atteint progressivement une stœchiométrie idéale (de 53,16 % à 51,19 %) parallèlement au développement de la dolomitisation. Les dolomites du Lettenkohle montrent une stœchiométrie proche d’une stœchiométrie idéale (51,06 % Ca), sont ordonnées et associées à de l’anhydrite. Leur formation est liée à deux étapes de dolomitisation : de type sabkha et d’enfouissement. Cette étude permet ainsi une meilleure caractérisation des différents types de dolomites dans les roches sédimentaires et par conséquent une meilleure détermination de leur potentiel en tant que réservoir.

Abstract — Empirical Calibration for Dolomite Stoichiometry Calculation: Application on Triassic Muschelkalk-Lettenkohle Carbonates (French Jura) — This study concerns an approach for dolomite quantification and stoichiometry calculation by using X-ray diffractometry coupled with cell and Rietveld refinements and equipped with a newly substantial database of dolomite composition. A greater accuracy and precision are obtained for quantifying dolomite as well as other mineral phases and calculating dolomite stoichiometry compared to the classical “Lumsden line” and previous methods. The applicability of this approach is verified on dolomite reference material (Eugui) and on Triassic (Upper Muschelkalk-Lettenkohle) carbonates from the French Jura. The approach shown here is applicable to bulk dolostones as well as to specific dolomite cements and was combined with petrographical and isotopic analyses.
Upper Muschelkalk dolomites were formed during burial dolomitization under fluids characterized by increased temperature and variable isotopic composition through burial. This is clear from their Ca content in dolomites which gradually approaches an ideal stoichiometry (from 53.16% to 51.19%) through increasing dolomitization. Lettenkohle dolostones consist of near-ideal stoichiometric (51.06%Ca) and well-ordered dolomites associated with anhydrite relics. They originated through both sabkha and burial dolomitization. This contribution gives an improved method for the characterization of different dolomite types and their distinct traits in sedimentary rocks, which allows a better evaluation of their reservoir potential.

INTRODUCTION

Ideal dolomite has a crystal lattice consisting of alternating layers of Ca and Mg, separated by layers of CO₃, and is typically represented by a stoichiometric chemical composition of CaMg(CO₃)₂ where calcium and magnesium are present in equal proportions (Reeder, 1990). Most of the properties of carbonate rocks (limestone and dolostone) are primarily defined during their deposition and subsequent early diagenesis. With reference to dolostones, rock properties tend to change with time and particularly so during mesogenesis (shallow marine to deep burial; Land, 1980). Commonly, these diagenetic stages represent an overprint of the previous depositional or early diagenetic events. Cation substitutions in the crystal lattice, in particular Ca and Mg, through dissolution-precipitation reactions, change the stoichiometry of the dolomite. As a result, dolomite exhibits variation in chemical composition and in atomic arrangements (Reeder, 1981; Hardie, 1987).

Very few sedimentary dolomites are truly stoichiometric (CaMg(CO₃)₂). They are better represented as:

\[ \text{Ca}_{x+y} \text{Mg}_{1-x} (\text{CO}_3)_{2} \]

typically with more Ca than Mg (Goldsmith and Graf, 1958; Lumsden, 1979; Searl, 1994; Budd, 1997). Therefore, the term “dolomite” describes a mineral series of carbonate that encompass a range of chemical variation and lattice structures. The stoichiometry, the texture and possible association with evaporates are generally used to identify different types of dolomite in sedimentary rocks (Morrow, 1978, 1982a; Lumsden and Chimahusky, 1980). This can also reveal diagenetic environmental settings that affected dolomite formation (Mattes and Mountjoy, 1980; Morrow, 1982; Machel and Mountjoy, 1986). Non-stoichiometric dolomite crystals are thermodynamically metastable under sedimentary conditions and therefore more reactive to diagenetic environments relative to “ideal” dolomites (Carpenter, 1980; Land, 1980; Lumsden and Chimahusky, 1980; Hardie, 1987; Vahrenkamp and Swart, 1994; Chai et al., 1995; Budd, 1997). For this reason, a burial trend towards stoichiometry exists (Land, 1980; Morse and Mackenzie, 1990). By knowing the “degree” of stability of dolomites (through stoichiometry) a more quantitative prediction whether the dolomite rock texture is prone for further changes – that may alter its reservoir properties such as porosity and permeability – is feasible.

X-Ray Diffractometry (XRD) is commonly used for measuring the crystallographic structure and the stoichiometry of dolomites. The Ca/Mg ratio of a dolomite is classically determined from the displacement of the d₁₀₄ main dolomite reflection. Lumsden (1979) established an equation linking molar content of CaCO₃ in dolomite to the d₁₀₄ spacing measured on XRD profiles. Several authors have shown that dolostones can diverge from the Lumsden line (Reeder and Sheppard, 1984; Kimbell, 1993; Jones et al., 2001).

This paper presents an empirical calibration for the assessment of stoichiometry and crystal lattice properties of dolomite based on XRD peaks. Dolomite crystals lattice parameters (a = b and c in Å in a rhombohedral crystal system) are determined by unit cell refinement, and by using a newly compiled database of dolomite composition. From these the related %Ca of the analyzed dolomites could be estimated. This approach yielded a better accuracy and precision than the previous methods. In addition, it is a rapid and inexpensive technique which only requires a small amount of sample. Hence, it allows for quantifying dolomite stoichiometry of bulk sediments as well as cements. This workflow also results in a mineralogical quantification of the coexisting phases in the samples based on the Rietveld refinement.

1 STUDY LOCALITY AND MATERIAL

The direct applicability of the presented approach is demonstrated on Triassic carbonates (Upper Muschelkalk and Lettenkohle Formation) from the Chatelblanc 1 borehole located in the French Jura (Fig. 1). The Triassic is a period of transition associated with the beginning of the break-up of the Pangean supercontinent and the development of the Mesozoic basins. The Germanic facies province is characterized by a tripartite subdivision of the Triassic series (Ziegler, 1982) into the Scythian, the Anisian and Ladinian (including Muschelkalk carbonates and evaporates), and the Carnian to Norian (including Lettenkohle Formation). At the onset of the Late Ladinian, open-marine, clear water conditions induced the development of extensive carbonate platforms,
these grade westwards and northwards into dolomitic and evaporitic clays (Wolburg, 1969; Senkowiczowa and Szyperko-Silwczynska, 1975; Alten et al., 1980). The Jura Mountain range is a small, arcuate fold belt forming the frontal portion and the youngest deformation zone (from Middle Miocene onward) of the northwestern Alpine arc surrounded by Tertiary basins (Fig. 1). The Chatelblanc region is situated in the Haute Chaîne Jura of France (Fig. 1). The landscape of this area consists of folded mounts with a general NE-SW direction. The Chatelblanc 1 borehole is located on an anticlinal axis NE-SW corresponding to the front of the Haute Chaîne Jura which overlaps the Nozeroy Plateau (Fig. 1). The carbonate rock series of Upper Muschelkalk and Lettenkohle Formation are surrounded by two levels of decollement and are poorly or not affected by alpine compressive tectonic.

Forty carbonate samples from the Chatelblanc 1 borehole were collected from three core segments (No. 2, 3 and 4). Seventeen samples were taken from the Upper Muschelkalk (core segments 3 and 4 ranging from 2,289 m to 2,297 m depth), and twenty-three from the Lettenkohle Formation (core segment 2 ranging from 2,267 m to 2,277 m depth). The Upper Muschelkalk sedimentary rocks (limestones and dolostones) consist of mudstones, bioclastic wackestones and grainstones with rare evaporite nodules, while Lettenkohle sedimentary rocks are characterized by a succession of mudstones and evaporites (beds or displacive nodules of anhydrite) with some clay layers (see Fig. 3 in Sect. 4.1.1). Their facies are characteristic of a shallow lagoon environment.

2 METHODS

2.1 X-Ray Diffractometry and Refinements

Each dry sample was uniformly ground in an agate mortar for XRD measurements. Alumina standard material (NIST) was added to each powder sample as an internal standard (50 wt%) and the mixture was again ground for few minutes until homogeneous. The Alumina cell parameters were taken from the NIST information file (SRM 676a). XRD patterns were collected using Cu radiation, from 0° to 80° 2θ with a 0.017° 2θ step size and 91 s. 2θ-1 counting time with a position-sensitive detector on an X'pertPro Panalytical diffractometer. The identification of minerals was performed on the measured digitized diffractograms, using the ICDD database (PDF4+). XRD analyses in 0-2θ configuration were undertaken with a parallel beam focused by an elliptic W/Si crystal...
mirror. The measurements were performed on the samples in holders (several g of powder) and also enclosed in a 1 mm glass capillary (0.1 g of powder).

Structure and cell refinements were performed on the resulting diagrams with HighScore Plus 2.2 software. The structure refinement method is based on a least-squares refinement procedure. This approach allows for a quantitative assessment of the agreement between observed and calculated integrated intensities by refining structural parameters (Rietveld, 1969). Based on all measured diffraction peaks, Rietveld refinement is used to quantify the relative proportions of coexisting phases in samples. Cell refinement was used to determine the unit cell parameters of the dolomite crystals. The peak positions of the NIST Alumina are used to correct the peak shift error (in two-theta) of the powder diagrams. The instrumental characteristics of the diffractometer, influencing peak shapes, have been taken into account for the refinement with Caglioti coefficients optimized (\( U = 0.07509, V = -0.05312 \) and \( W = 0.03425 \)) on powder mineral standards (alumina, calcite, zinc oxide, quartz, molybdenite, muscovite). The relative error on quantification via Rietveld refinement was calculated for common minerals (Kohler et al., 2009).

The uncertainty for non-clay phases is logically linked to the phase proportion in the sample. When the abundance is equal to 5%, the associated uncertainty is 60% while it decreases at 10% when the proportion is equal to 30%. Abundances higher than 40% are related to uncertainties less than 5%.

### 2.2 Petrography and Stable (C and O) Isotope Ratios

Samples were subjected to petrographic observations including conventional and cathodoluminescence (CL) microscopy (Cathodyne OPEA; operation conditions were 14 to 16 kV gun potential, 500 to 600 µA beam current, 0.05 torr vacuum).

The various carbonate (calcite and dolomite) phases (matrix and cements) were micro-sampled (using a dentist’s micro-drill) for measuring their carbon and oxygen stable isotope composition. Analyses were carried out at the University of Erlangen, Germany. During this process, the carbonate powders were reacted with 100% phosphoric acid (density \( > 1.9 \); Wachter and Hayes, 1985) at 75°C in an online carbonate preparation line (Carbo-Kiel – single sample acid bath) connected to a ThermoFinnigan 252 mass-spectrometer (Thermo Electron Corp., Waltham, MA, USA). All values are reported in per mill relative to Vienna Pee Dee Belemnite (Thermo Electron Corp., Waltham, MA, USA). All values are connected to a ThermoFinnigan 252 mass-spectrometer (ThermoFinnigan 252 mass-spectrometer). The instrumental characteristics of the diffractometer, influencing peak shapes, have been taken into account for the refinement with Caglioti coefficients optimized (\( U = 0.07509, V = -0.05312 \) and \( W = 0.03425 \)) on powder mineral standards (alumina, calcite, zinc oxide, quartz, molybdenite, muscovite). The relative error on quantification via Rietveld refinement was calculated for common minerals (Kohler et al., 2009).

The uncertainty for non-clay phases is logically linked to the phase proportion in the sample. When the abundance is equal to 5%, the associated uncertainty is 60% while it decreases at 10% when the proportion is equal to 30%. Abundances higher than 40% are related to uncertainties less than 5%.

### 3 EMPIRICAL APPROACH FOR STOICHIOMETRY ASSESSMENT OF DOLOMITES

#### 3.1 Stoichiometry Calculation

A pioneering technique for the calculation of the dolomite crystal stoichiometry (%mol CaCO\(_3\)) was established by Lumsden (1979), who used the relationship between the calcium content and the measured \( d_{104} \) spacing on X-ray profiles. Calcium in excess of stoichiometry (Ca\(_{50}\)Mg\(_{50}\)) increases the \( d_{104} \) distance of dolomite as a linear function of the excess Ca amount (Goldsmith and Graf, 1958; Runnels, 1970; Lumsden, 1979). Lumsden (1979) used two \( d_{104} \) data points (Ca\(_{95}\)Mg\(_{5}\) and Ca\(_{90}\)Mg\(_{10}\)) determined by Goldsmith and Graf (1958) to derive the linear relationship between \( d_{104} \) and composition: \( N_{\text{CaCO}_3} = M \times d_{104} + B \) (with \( N_{\text{CaCO}_3} \): CaCO\(_3\) percent in dolomite, \( d_{104} \): observed \( d_{104} \) value, \( M = 333.33 \) and \( B = -911.99 \)). The standard error is ±0.15% on the mean composition with this procedure and the maximum difference for a given \( d_{104} \) value, based on the “Lumsden line”, is about 1.45%Ca. Reeder and Sheppard (1984), Kimbell (1993) and Jones et al. (2001) reporting on the \( d_{104} \) value and the average %Ca (measured by electron microprobe) documented that Ca-rich dolostones differ significantly from the “Lumsden line” and could commonly deviate in the order of 4-5%Ca (Jones et al., 2001). These authors assign such discrepancies to a significant difference between the percentage of Ca atoms per formula unit determined by electron microprobe analysis and by XRD. Hence, Jones et al. (2001) have proposed a means of determining stoichiometries and abundances of dolomite phase based on a XRD peak fit method focusing on the \( d_{104} \) peak.

The study presented here develops an empirical calibration for calculating the dolostones stoichiometry based on the determination of the unit cell parameters of the dolomite crystals. It is based on the Rietveld technique, not solely on the dolomite main diffraction peak (\( d_{104} \), as the classical Lumsden equation or as the peak fit method of Jones et al. (2001), but on several dolomite diffraction peaks. According to a unit cell refinement (crystal lattice deformation), this approach gives access to the lattice parameters of dolomite crystals \( (a = b \) and \( c \) in Å). Using a new database of dolomite compositions as a function of lattice parameters allows calculating the %Ca in dolomites. This database is based on a comprehensive literature review. It is compiled from the crystallographic characteristics (cell parameters related to the lattice Ca percentage) of ninety-eight natural dolomites (Tab. 1). Dolomites solely composed of Ca and Mg (no Fe and Mn, except for the well studied Eugui reference) have been considered in order to test the method in a simpler case study. Depending on the authors, stoichiometry of these natural dolomites has been determined by four distinct methods (X-ray refinement, electron microprobe analysis, X-ray fluorescence spectroscopy analysis, Lumsden equation; Tab. 1) associated with an own...
Crystallographic characteristics (cell parameters related to the lattice Ca and Mg percentages) of 98 natural dolomites. Dolomites only composed by Ca and Mg have been considered for this study (except the largely studied Eugui sample which contains also Fe and Mn). Stoichiometry of these dolomites has been determined by four distinct methods (X-ray fluorescence spectroscopy analysis, X-ray refinement, electron microprobe analysis, Lumsden equation). Authors, age and location of dolomite samples are also indicated.

| Dolomite studies         | Age          | Location sample | Method       | a = b (Å) | c (Å)   | %mol Ca |
|--------------------------|--------------|-----------------|--------------|-----------|---------|---------|
| Reeder and Wenk (1983)  | Carboniferous| Eugui, Spain    | XRF analysis | 4.8038    | 16.006  | 50.05   |
| McCarty et al. (2006)   | Carboniferous| Eugui, Spain    | XRF analysis | 4.8078    | 16.002  | 50.06   |
| McCarty et al. (2006)   | Mississippian| Uinta County, USA| XRF analysis | 4.8086    | 16.0129 | 50.85   |
| McCarty et al. (2006)   | Mississippian| Uinta County, USA| XRF analysis | 4.8116    | 16.0251 | 51.35   |
| McCarty et al. (2006)   | Mississippian| Uinta County, USA| XRF analysis | 4.8119    | 16.0278 | 51.35   |
| McCarty et al. (2006)   | Mississippian| Uinta County, USA| XRF analysis | 4.8123    | 16.0238 | 52      |
| McCarty et al. (2006)   | Mississippian| Uinta County, USA| XRF analysis | 4.8115    | 16.0311 | 52.05   |
| McCarty et al. (2006)   | Mississippian| Uinta County, USA| XRF analysis | 4.8096    | 16.0213 | 51.65   |
| McCarty et al. (2006)   | Mississippian| Uinta County, USA| XRF analysis | 4.809     | 16.0191 | 50.95   |
| McCarty et al. (2006)   | Mississippian| Uinta County, USA| XRF analysis | 4.8104    | 16.0248 | 51.45   |
| McCarty et al. (2006)   | Mississippian| Uinta County, USA| XRF analysis | 4.8095    | 16.0211 | 51.45   |
| McCarty et al. (2006)   | Mississippian| Uinta County, USA| XRF analysis | 4.809     | 16.0139 | 50.7    |
| McCarty et al. (2006)   | Permian      | Lea County, USA  | XRF analysis | 4.8127    | 16.0476 | 52.3    |
| McCarty et al. (2006)   | Permian      | Lea County, USA  | XRF analysis | 4.8126    | 16.0455 | 52.4    |
| McCarty et al. (2006)   | Permian      | Lea County, USA  | XRF analysis | 4.8137    | 16.0536 | 53.15   |
| McCarty et al. (2006)   | Permian      | Lea County, USA  | XRF analysis | 4.813     | 16.0368 | 52.35   |
| McCarty et al. (2006)   | Permian      | Lea County, USA  | XRF analysis | 4.8138    | 16.0517 | 52.5    |
| McCarty et al. (2006)   | Permian      | Lea County, USA  | XRF analysis | 4.8129    | 16.0575 | 52.65   |
| McCarty et al. (2006)   | Permian      | Lea County, USA  | XRF analysis | 4.8082    | 16.0101 | 50.3    |
| McCarty et al. (2006)   | Permian      | Lea County, USA  | XRF analysis | 4.8083    | 16.0105 | 50.4    |
| McCarty et al. (2006)   | Permian      | Lea County, USA  | XRF analysis | 4.8082    | 16.0077 | 50.1    |
| McCarty et al. (2006)   | Permian      | Lea County, USA  | XRF analysis | 4.8089    | 16.015  | 50.6    |
| McCarty et al. (2006)   | Permian      | Lea County, USA  | XRF analysis | 4.8123    | 16.0295 | 52.85   |
| McCarty et al. (2006)   | Permian      | Lea County, USA  | XRF analysis | 4.8128    | 16.0364 | 52.85   |
| McCarty et al. (2006)   | Permian      | Lea County, USA  | XRF analysis | 4.8144    | 16.0597 | 53.4    |
| McCarty et al. (2006)   | Permian      | Lea County, USA  | XRF analysis | 4.8123    | 16.0391 | 52.4    |
| McCarty et al. (2006)   | Permian      | Lea County, USA  | XRF analysis | 4.8126    | 16.0403 | 52.95   |
| McCarty et al. (2006)   | Permian      | Lea County, USA  | XRF analysis | 4.8129    | 16.0459 | 52.85   |
| McCarty et al. (2006)   | Permian      | Lea County, USA  | XRF analysis | 4.8122    | 16.0422 | 52.2    |
| McCarty et al. (2006)   | Permian      | Lea County, USA  | XRF analysis | 4.813     | 16.0496 | 52.9    |
| McCarty et al. (2006)   | Permian      | Lea County, USA  | XRF analysis | 4.814     | 16.0569 | 52.9    |
| McCarty et al. (2006)   | Permian      | Lea County, USA  | XRF analysis | 4.8142    | 16.0595 | 53.4    |
| McCarty et al. (2006)   | Permian      | Lea County, USA  | XRF analysis | 4.8138    | 16.0502 | 52.8    |
| McCarty et al. (2006)   | Permian      | Lea County, USA  | XRF analysis | 4.8128    | 16.0458 | 52.9    |
| McCarty et al. (2006)   | Permian      | Lea County, USA  | XRF analysis | 4.8157    | 16.0581 | 53.55   |
| McCarty et al. (2006)   | Permian      | Lea County, USA  | XRF analysis | 4.8151    | 16.0506 | 53.15   |
| McCarty et al. (2006)   | Permian      | Lea County, USA  | XRF analysis | 4.8136    | 16.0526 | 52.75   |
| McCarty et al. (2006)   | Permian      | Lea County, USA  | XRF analysis | 4.8138    | 16.0498 | 53      |
| McCarty et al. (2006)   | Permian      | Lea County, USA  | XRF analysis | 4.815     | 16.0586 | 53.4    |
| McCarty et al. (2006)   | Permian      | Lea County, USA  | XRF analysis | 4.8122    | 16.06   | 52.5    |
| McCarty et al. (2006)   | Permian      | Lea County, USA  | XRF analysis | 4.8134    | 16.0533 | 52.6    |
| McCarty et al. (2006)   | Permian      | Lea County, USA  | XRF analysis | 4.8132    | 16.048   | 52.85   |
| McCarty et al. (2006)   | -            | -               | XRF analysis | 4.8085    | 16.0113 | 50.8    |
| McCarty et al. (2006)   | -            | -               | XRF analysis | 4.8111    | 16.0245 | 51.25   |
| McCarty et al. (2006)   | -            | -               | XRF analysis | 4.8115    | 16.0266 | 51.55   |
| McCarty et al. (2006)   | -            | -               | XRF analysis | 4.8119    | 16.0217 | 51.4    |
| McCarty et al. (2006)   | -            | -               | XRF analysis | 4.8125    | 16.0312 | 52      |
| McCarty et al. (2006)   | -            | -               | XRF analysis | 4.8122    | 16.0249 | 51.4    |
| Dolomite studies                  | Age          | Location sample    | Method      | $a = b$ (Å) | $c$ (Å) | %mol Ca |
|----------------------------------|--------------|--------------------|-------------|-------------|---------|---------|
| Reeder and Wenk (1983)           | Carboniferous| Eugui, Spain       | X-ray refinement | 4.8038 | 16.006 | 50.5    |
| Drits et al. (2005)              | Permian      | Lea County, USA    | X-ray refinement | 4.814   | 16.041 | 54      |
| Drits et al. (2005)              | Permian      | Lea County, USA    | X-ray refinement | 4.8274  | 16.137 | 58.5    |
| Drits et al. (2005)              | Permian      | Lea County, USA    | X-ray refinement | 4.8141  | 16.039 | 53.5    |
| Drits et al. (2005)              | Permian      | Lea County, USA    | X-ray refinement | 4.8247  | 16.124 | 56.5    |
| Drits et al. (2005)              | Aptian       | Coke County, USA   | X-ray refinement | 4.8114  | 16.025 | 53.5    |
| Drits et al. (2005)              | Aptian       | Coke County, USA   | X-ray refinement | 4.8215  | 16.111 | 57      |
| Althoff (1977)                   | -            | Binnenthal, Switz. | EMP analysis | 4.8033  | 15.984 | 50.5    |
| Navrotsky and Capobianco (1987)  | Carboniferous| Eugui, Spain       | EMP analysis | 4.8066  | 16.0016 | 50 |
| Goldsmith and Graf (1958)        | Eocene       | Lake Arthur, USA   | EMP analysis | 4.8069  | 16.0034 | 50.1 |
| Reeder (2000)                    | Eocene       | Florida, USA       | EMP analysis | 4.8201  | 16.072 | 54.5    |
| Reeder and Sheppard (1984)       | Eocene       | Florida, USA       | EMP analysis | 4.815   | 16.03  | 51.1    |
| Reeder and Sheppard (1984)       | Eocene       | Florida, USA       | EMP analysis | 4.814   | 16.031 | 51.5    |
| Reeder and Sheppard (1984)       | Eocene       | Florida, USA       | EMP analysis | 4.813   | 16.02  | 51.6    |
| Reeder and Sheppard (1984)       | Eocene       | Florida, USA       | EMP analysis | 4.815   | 16.035 | 52.5    |
| Reeder and Sheppard (1984)       | Eocene       | Florida, USA       | EMP analysis | 4.819   | 16.097 | 53.8    |
| Reeder and Sheppard (1984)       | Eocene       | Florida, USA       | EMP analysis | 4.829   | 16.14  | 55.6    |
| Reeder and Sheppard (1984)       | Eocene       | Florida, USA       | EMP analysis | 4.828   | 16.152 | 56      |
| Reeder and Sheppard (1984)       | Eocene       | Florida, USA       | EMP analysis | 4.831   | 16.134 | 55.7    |
| Reeder and Sheppard (1984)       | Eocene       | Florida, USA       | EMP analysis | 4.829   | 16.129 | 55.6    |
| Reeder and Sheppard (1984)       | Eocene       | Florida, USA       | EMP analysis | 4.82   | 16.085 | 54.3    |
| Reeder and Sheppard (1984)       | Eocene       | Florida, USA       | EMP analysis | 4.813   | 16.023 | 50.1    |
| Reeder and Sheppard (1984)       | Eocene       | Florida, USA       | EMP analysis | 4.83   | 16.143 | 56.2    |
| Reeder and Sheppard (1984)       | Eocene       | Florida, USA       | EMP analysis | 4.82   | 16.117 | 54.5    |
| Reeder and Sheppard (1984)       | Ordovician   | Wisconsin, USA     | EMP analysis | 4.814   | 16.03  | 51.2    |
| Reeder and Sheppard (1984)       | Ordovician   | Wisconsin, USA     | EMP analysis | 4.814   | 16.032 | 50.8    |
| Reeder and Sheppard (1984)       | Ordovician   | Wisconsin, USA     | EMP analysis | 4.816   | 16.032 | 50.8    |
| Reeder and Sheppard (1984)       | Ordovician   | Wisconsin, USA     | EMP analysis | 4.812   | 16.024 | 51.4    |
| Spötl and Burns (1991)           | Triassic     | Austria            | Lumsden equation | 4.8032  | 16.0175 | 51 |
| Spötl and Burns (1991)           | Triassic     | Austria            | Lumsden equation | 4.8076  | 15.9992 | 49 |
| Spötl and Burns (1991)           | Triassic     | Austria            | Lumsden equation | 4.8056  | 16.0116 | 50.7 |
| Spötl and Burns (1991)           | Triassic     | Austria            | Lumsden equation | 4.8035  | 16.0123 | 50    |
| Spötl and Burns (1991)           | Triassic     | Austria            | Lumsden equation | 4.8048  | 16.0106 | 49    |
| Spötl and Burns (1991)           | Triassic     | Austria            | Lumsden equation | 4.8066  | 16.0054 | 48.7 |
| Spötl and Burns (1991)           | Triassic     | Austria            | Lumsden equation | 4.8047  | 16.0141 | 50    |
| Spötl and Burns (1991)           | Triassic     | Austria            | Lumsden equation | 4.8077  | 16.0185 | 50    |
| Spötl and Burns (1991)           | Triassic     | Austria            | Lumsden equation | 4.8038  | 16.0119 | 49    |
| Spötl and Burns (1991)           | Triassic     | Austria            | Lumsden equation | 4.8062  | 16.0103 | 49.7 |
| Spötl and Burns (1991)           | Triassic     | Austria            | Lumsden equation | 4.8053  | 16.0163 | 49.7 |
| Spötl and Burns (1991)           | Triassic     | Austria            | Lumsden equation | 4.8033  | 16.0149 | 49.7 |
| Spötl and Burns (1991)           | Triassic     | Austria            | Lumsden equation | 4.8047  | 16.0065 | 49.3 |
| Spötl and Burns (1991)           | Triassic     | Austria            | Lumsden equation | 4.808   | 16.0205 | 50.3 |
| Spötl and Burns (1991)           | Triassic     | Austria            | Lumsden equation | 4.8093  | 16.0226 | 51    |
| Spötl and Burns (1991)           | Triassic     | Austria            | Lumsden equation | 4.8075  | 16.0302 | 51.7 |
| Spötl and Burns (1991)           | Triassic     | Austria            | Lumsden equation | 4.806   | 16.0126 | 50.7 |
| Spötl and Burns (1991)           | Triassic     | Austria            | Lumsden equation | 4.8091  | 16.0147 | 51.3 |
| Spötl and Burns (1991)           | Triassic     | Austria            | Lumsden equation | 4.8057  | 16.0146 | 50.7 |
| Spötl and Burns (1991)           | Triassic     | Austria            | Lumsden equation | 4.8053  | 16.0062 | 50    |
| Spötl and Burns (1991)           | Triassic     | Austria            | Lumsden equation | 4.8051  | 16.0121 | 49.7 |
standard deviation on the %Ca calculation. Some of these studies include dolomites with a small %Ca range (Spötl and Burns; 1991; McCarty et al., 2006). However, they have been considered in order to propose an extensive database. From the collected data, two linear regressions can be calculated. A first one links the \(a (= b)\) crystallographic parameter to the %mol CaCO\(_3\) in dolomite and a second one the \(c\) crystallographic parameter to the %mol CaCO\(_3\) in dolomite (Fig. 2).

A natural and nearly stoichiometric dolomite from the metamorphic carbonate complex of Eugui in Spain, extensively characterized (Barber et al., 1981; Reeder and Nakajima, 1982; Reeder and Wenk, 1983; Reeder and Markgraf, 1986; Navrotsky and Capobianco, 1987), was used as a comparative standard. The Eugui sample was used to test the reproducibility and the accuracy of the method proposed in this study for both lattice parameters refinement and stoichiometry calculation. The cell refinement analysis on the Eugui dolomite reference sample gives mean lattice parameters values of \(a (= b) = 4.8074(7) \text{ Å}\) and \(c = 16.013(1) \text{ Å}\). The Eugui sample stoichiometry calculation based on the linear regressions from the database of dolomite compositions (Fig. 2) has a mean value of 50.69%Ca (50.70% on average based on the \(a (= b)\) equation and 50.69% on average based on the \(c\) equation). The electron microprobe analysis made on the Eugui sample provides a mean composition of 51.3%mol Ca, 47.3%mol Mg, 1.2%mol Fe and 0.2%mol Mn (Ca\(_{1.03}\)Mg\(_{0.95}\)Fe\(_{0.02}\)Mn\(_{0.004}\)(CO\(_3\))\(_2\)). Analysis of the sample using the traditional Lumsden equation provides a mean value of 50.37%Ca. Barber et al. (1981), Reeder and Wenk (1983) and Jones et al. (2001) using other Eugui samples obtained a mean value of 50.4%Ca (Peakfit-XRD and EMP). Eugui sample analysis demonstrates that the uncertainty on the stoichiometry calculation using the approach presented in this study is related to the empirical calibration. The determination of lattice parameters values via the cell refinement is very accurate. It provides stoichiometry with a standard deviation estimated to be within ±0.05% and ±0.04% from \(a (= b)\) and \(c\) linear regressions respectively, and ±0.01% for the mean stoichiometry value from both linear regressions. The uncertainty related to the empirical calibration results in %Ca values deviating on average of ±1.90% and ±1.56% using \(a (= b)\) and \(c\) linear regressions respectively, at the 95% confidence level (Fig. 2). Hence, the %Ca difference for Eugui sample between values determined by this procedure (50.70%) and by EMP (51.30%) in this study is thus within the uncertainty interval.
3.2 Comparison with Previous Studies

Jones et al. (2001) have developed a dolomite stoichiometry calculation based on a X-ray peak fit method on multi-phases dolomites. Lettenkohle and Upper Muschelkalk dolomites used here for application correspond to the matrix of dolostones. They are related to uniform and symmetrical diffraction peaks and do not show composite peak-forms (produced by the superposition of two peaks; see Jones et al., 2001 and Drits et al., 2005). If stoichiometric differences exist within samples (due to various populations of dolomite crystals), the difference is too small to be observed on the measured diffraction peaks of dolomite. Dolomites analyzed from Lettenkohle and Upper Muschelkalk are thus considered as mono-phase dolomites. It is feasible to determine the lattice parameters of multi-phases dolomites by cell refinement, however it couldn’t be tested on the French Jura Triassic mono-phase dolomites. It is then difficult to compare accuracies on stoichiometry results from the Jones et al. (2001) method with the approach of the present study. However, Jones et al. (2001) looked only at the position and profile of \(d_{104}\) while the Rietveld and unit cell refinements used here are considering several dolomite diffraction peaks, providing a better accuracy and precision on results.

The study of McCarty et al. (2006) concerns dolomite stoichiometry and quantification of mono and two-phases samples using refinements on dolomite diffraction peaks. It also provides two linear equations relating \(a\) or \(c\) parameter to Ca content based on a combined X-ray, ICP-AES and XRF study. Based on the cell parameters values and the \(d_{104}\) peak position determined in the present study, stoichiometry of Eugui dolomite has been calculated with the Lumsden (1979) method with the approach presented here is consistent with the micro-probe analysis and the previous studies (Barbet et al., 1981; Reeder and Wenk, 1983; Jones et al., 2001). Therefore, this method can be equally applied to dolomites having few percent of Fe and Mn in their lattices. However, the %Ca calculated on Eugui dolomite by the approach presented here is consistent with the micro-probe analysis and the previous studies (Barbet et al., 1981; Reeder and Wenk, 1983; Jones et al., 2001). Therefore, this method can be equally applied to dolomites having few percent of Fe and Mn in their lattices. Care must be taken, however, when dolomites display higher Fe and Mn contents and tend toward the ankerite pole.

4 APPLICATION ON TRIASSIC CARBONATES OF THE FRENCH JURA

4.1 Characterization of Sediments

4.1.1 Mineral Quantification

The main components of Upper Muschelkalk sedimentary rocks are both dolomite and calcite (Fig. 3). Quartz, feldspars, anhydrite, felspathoids and others minerals occur in minor or trace proportions. The main constituents of Lettenkohle sedimentary rocks are anhydrite and dolomite (Fig. 3). These

| Table 2 |

| Table 2: Mean stoichiometry value and Standard Deviation associated (SD) of Eugui sample calculated from different linear regression equations. The \(d_{104}\) position and the unit cell values are from this study. |

| Eugui samples | \(d_{104}\) (Å) | \(c\) (Å) | Ca (%mol) with \(a = b\) | Ca (%mol) with \(c\) | Mean %Ca | Linear regression equations from |
|---------------|----------------|-----------|---------------------------|---------------------------|--------------|---------------------------------|
| Average SD    | 2.8871         | 16.013(1) | 50.70                     | 50.69                     | 50.69        | This study                       |
| Average       | 0.0013         | 0.00025   | 0.07                      | 0.06                      | 0.01         |
| Average       | 50.16          | 50.57     | 50.37                     | 50.37                     | 50.37       | McCarthy et al. (2006)          |
| SD            | 0.11           | 0.08      | 0.02                      |                           |
| Average       | 50.37          |          |                           |                           |             | Lumsden (1979)                 |
| SD            | 0.42           |          |                           |                           |             |                                 |
Figure 3

Detailed lithological log of the Upper Muschelkalk (core segments 3 and 4) and Lettenkohle Formation (core segment 2) of the Chatelblanc 1 borehole. Sampling, depth, structure and texture are indicated. Mineralogical quantification of limestones and dolostones is also given. Lithology is based on macroscopically observations while mineral quantification has been determined by X-ray diffractometry. The dashed line represents the log continuity with a gap in thickness indicated by depth values.
mineralogies alternate with intervals composed of quartz, feldspars, micas, chlorite group minerals and pyrite.

4.1.2 Petrographic Description and Paragenesis

The Upper Muschelkalk carbonate facies include two types of matrix (low-magnesium calcite and dolomite), three types of dolomite cements and three types of low-magnesium calcite cements (Fig. 4, 5). The original lime-micritic matrix (CM) is completely or partially preserved in samples. Original calcite crystals form the foliated and prismatic structures of brachiopod shells whereas Calcite Cement 1 (CC1) is a mimetic replacement of precursor aragonite in bivalve shells (Fig. 4b). Calcite Cement 2 (CC2) fills biomoldic pores (Fig. 4e) and also occurs in rare vugs. Calcite Cement 3 (CC3) fills fractures and occasionally veins (Fig. 4d). The Dolomite Matrix (DM) is characterized by rhombs with an average size less than 20 μm, floating in the micritic limestone matrix (Fig. 4). According to the classification proposed by Sibley and Gregg (1987), this dolomite is defined by a unimodal texture and euhedral (planar-e type) to subhedral (planar-s type) rhombs. Dolomite Cement 1 (DC1) consists of a unimodal planar-e texture with crystals size ranging from 15 to 75 μm (Fig. 4c). Dolomite Cement 2 (DC2) occurs in biomolds and in rare vugs, is associated with CC2 (Fig. 4e) and defined by a polymodal texture and euhedral (planar-e type) crystals. Dolomite Cement 3 (DC3) is a blocky cement which fills fractures and rarely veins. It shows a polymodal planar-s texture composed by non-luminescent crystals with a size ranging from 50 to 1 500 μm. Fractures are filled either with CC3 or DC3 but never with both mineralogies. All dolomites have a mottled-red luminescence in CL, except DC3. A relatively uniform Dolomite Matrix and two types of dolomite cements are distinguished in Lettenkohle sediments (Fig. 5, 6). The Dolomite Matrix (DM) is defined by a unimodal texture and subhedral (planar-s type) rhombs, whose size is less than 20 μm. The matrix dolomite rhombs have a bright orange CL-pattern with a diffuse zonation (cloudy centres surrounded by clear rims; Fig. 5a). The Dolomite Cement 1 (DC1) occurs in rare vugs and has a polymodal planar-s texture composed by non-luminescent crystals with a size ranging from 15 to 150 μm (Fig. 5b). The Dolomite Cement 2 (DC2) is characterized by a blocky cement type (Fig. 5c, d). Dolomite crystals of this fracture-filling cement are defined by a polymodal planar-s texture, are non-luminescent under CL viewing and have sizes ranging from 50 to 1 500 μm.

The petrographic relationships between these various calcite and dolomite phases shed light on the relative timing of their formation (Fig. 5). In the Upper Muschelkalk sedimentary rocks, the paragenesis proposed is based on the following arguments:

- the crosscutting of CC1 by DC1 suggests an early precipitation of CC1;
- the crosscutting of DC1 by CC1 indicates the previous occurrence of DC1;
- the corrosion of DC2 by CC2 favours an earlier precipitation of DC2;
- the crosscutting of all structures by fractures and veins, filled with CC3 or DC3, implies that they represent the latest carbonate precipitation.

Evidence for a chronology between CC3 and DC3 is lacking. In the Lettenkohle sedimentary rocks:

- the alternation of Dolomite Matrix (DM) and anhydrite (laminated macro- and microscopically) suggests their concomitant precipitation;
- the DM corrosion by anhydrite (irregular nodules macro- and microscopically) indicates a previous formation of the matrix;
- the crosscutting of all structures by the fractures and veins (except anhydrite with a regular nodule form macro- and microscopically), filled with DC2, suggests that DC2 represents the latest dolomite precipitation.

4.1.3 Description of Carbon and Oxygen Stable Isotopic Compositions

The isotopic ratios from well-preserved Middle Triassic brachiopods (low-magnesium calcite) represent the seawater composition (Korte et al., 2005; Fig. 7). Marine dolomite δ18O must not be directly compared with marine calcite δ18O as the equilibrium fractionation between dolomite and water at low temperature is debatable (Land, 1980). A common method to avoid this problem is to calculate the equilibrium isotopic composition of calcite for a particular fluid and temperature, and then to assume a geologically reasonable value for Δ18O_{dol-cal} (= δ18O_{dol} − δ18O_{calc} - V-PDB), in order to derive an estimate of the equilibrium isotope composition of dolomite from that fluid at that temperature. A mean value of Δ18O_{dol-cal} widely accepted to determine the marine dolomite signature, and applied here, is 3‰ (Budd, 1997; Fig. 7). Upper Muschelkalk isotope ratios show a fairly tight fit of both calcite and dolomite along a linear trend (correlation coefficient R2 = 0.66) while Lettenkohle dolomite values are more variable. The δ18O and δ13C values of Calcite Matrix (CM) of the Upper Muschelkalk range from −6.2 to −2.2‰ and from 0 to +1.3‰ respectively, while calcite multi-phases samples (CM + CC1 + CC2) shows δ18O values between −6.7 and −4‰ and δ13C ratios from +0.2 to +1.1‰. Both matrix and multi-phase Upper Muschelkalk samples show the same covariance in δ18O and δ13C. The Upper Muschelkalk calcite cement occurring as fracture infilling (CC3) lies off that covariant trend and shows lighter δ18O (−8.0‰) and δ13C (0‰) values. Muschelkalk Dolomite Matrix (DM) displays δ18O ratios from −7.8 to −3.8‰ and δ13C between 0 and +1.3‰. The Upper Muschelkalk dolomite multi-phases samples (DM + DC1 + DC2) have δ18O values ranging from −8.3 to −5.6‰ and δ13C values between +0.2 and +1.1‰.
Figure 4

Transmitted light (coloured with alizarin red S and potassium ferricyanide) and CL photomicrographs of Upper Muschelkalk Chatelblanc 1 samples: a) CL photomicrograph of sample 3-8c showing the dull brown luminescent Calcite Matrix (CM) (top right), the Dolomite Matrix (DM) with a mottled red luminescence and bioclasts formed by the dull brown luminescent calcite (bottom left), separated by a stylolite filled by clays; b) plane-polarized photomicrograph of sample 3-8b showing the CM partially replaced by a DM and the Calcite Cement 1 (CC1) which mimics original bioclasts structure; c) plane-polarized photomicrograph of sample 4-5e showing the DM floating in the CM, the DC1, the Dolomite Cement 1 (DC1; white arrow) and biomold quartz filling (black arrow); d) plane-polarized photomicrograph of sample 4-5e showing CM, DM, CC1 and the blocky calcite cement (CC3) which fills fractures and veins; e) plane-polarized/CL photomicrograph-pair of sample 4-5a showing CM, the dull brown luminescent Calcite Cement (CC2) and the mottled red luminescent Dolomite Cement 2 (DC2) replacing the original bioclasts structure.
Lettenkohle Dolomite Matrix (DM) shows δ¹⁸O values ranging from −4.4 to −1.9‰ and δ¹³C values between −2.6 and +0.1‰. A single fracture-filling Dolomite Cement 2 (DC2) displays more depleted δ¹⁸O (−7.5‰) and δ¹³C (−0.8‰) ratios.

4.2 Interpretation of Diagenetic Environments

The non-luminescent pattern of Upper Muschelkalk Calcite Matrix and Cements suggest that the fluids responsible of their precipitation were either oxidizing (hence no Mn²⁺ or Fe²⁺...
were available for incorporation into calcite), or were reducing but lacked a source of sufficient Mn$^{2+}$ to generate a luminescent phase, and alternatively the fluids contained so much Fe$^{2+}$ relative to Mn$^{2+}$ that any luminescence generated is completely quenched. The $\delta^{18}O$ signature of some of these calcites (CM, CC1 and CC2) is close to reconstructed Triassic marine calcite compositions (Fig. 7). This suggests that the fluid responsible for those precipitations most likely was seawater, at least for the calcite phases associated to the less depleted isotope values. Based on the paragenesis (Fig. 5), the fracture fill cement (CC3) represents the latest precipitation in sediments. CC3 is associated to the lowest $\delta^{18}O$ value indicating formation from warm (hot?) waters during burial. The decrease in $\delta^{18}O$ (Fig. 7) could thus be associated to an increase of temperatures of precipitation during burial. The positive $\delta^{13}C$ values, close to the predicted paleo-seawater composition (Fig. 7), suggest a local carbon source represented by the dissolution of marine carbonates. The decrease in $\delta^{13}C$ could be related to the increasing inputs of $^{13}C$ associated with organic matter alteration during burial. All of this results in a linear covariance in $\delta^{18}O$-$\delta^{13}C$ through burial. The mottled red luminescence of Upper Muschelkalk Dolomite Matrix and Cements (DC1 and DC2) indicates considerable amounts of Mn had to be present relative to Fe, pore waters had thus to be reducing. As dolomitization requires an ample Mg source, seawater could be the dolomitizing fluid. However, the dolomites are more depleted in $\delta^{18}O$ compared to the calcites and they differ substantially from the oxygen signature of predicted Triassic marine dolomites. If the dolomites are originated from seawater they should display a more enriched stable isotopic composition compared to the calcitic cements, which they do not (Fig. 7). Consequently, the Upper Muschelkalk dolomites must be

Figure 6
Transmitted light (coloured with alizarin red S and potassium ferricyanide) and CL photomicrographs of Lettenkohle Chatelblanc 1 samples: a) CL photomicrograph of sample 2-3b showing the Dolomite Matrix (DM) displaying a bright orange luminescence with cloudy centres surrounded by clear rims; b) CL photomicrograph of sample 2-3e showing the non-luminescent dolomite cement (DC1) in a vug; c, d) plane-polarized/CL photomicrograph-pair of sample 2-3e showing a non-luminescent blocky fracture-filling Dolomite Cement (DC2).
the result of the circulation of burial fluids. As with the calcites, the linear trend in dolomite $\delta^{18}O$ values is interpreted to reflect increasing temperature with increasing burial as dolomitization proceeded.

In Lettenkohle rocks, the co-occurrence of dolomite and anhydrite suggests a dolomite formation in an evaporative environment. In such environments, $^{16}$O is selectively removed by evaporation from the water body, so that the residual evaporated water is enriched in $^{18}$O (Epstein and Mayeda, 1953; Lloyd, 1966). As a result, $^{18}$O enriched values could indicate a dolomitization from higher salinity waters (Land, 1980). There is no simple relationship between isotopic composition and salinity, as interaction with the atmosphere and groundwater can decrease the degree of isotope enrichment (Major et al., 1992; Meyers et al., 1993) Fine-grained Lettenkohle dolomites (DM) do indeed have more positive $\delta^{18}O$ compositions and more variable $\delta^{13}C$ compositions compared to those of the Upper Muschelkalk matrix dolomites. Lettenkohle dolomite isotope values are more negative than what would even be expected for a dolomite from a Triassic seawater (Korte et al., 2005). Dark dashed line square symbolizes the predicted stable isotope record for dolomites precipitated with respect to the Triassic seawater ($\Delta^{18}O_{dol-cal} = +3%$; Budd, 1997).

4.3 Dolomite Stoichiometry

Several types of Dolomite Matrix and Cements, associated to different crystal sizes, have been underlined by petrography (Fig. 4-6). However, some carbonate phases couldn’t be micro-sampled as a single phase explaining the distinction between mono- and multi-phase samples (Fig. 7). For this reason, the stoichiometry calculated here is only associated to the Dolomite Matrix of samples. Only the DC2 in Lettenkohle have been micro-sampled as a single phase due to a sufficient amount of cement occurring in a large fracture (sample 2-3e). The resulting stoichiometric calculations from empirical calibration (Fig. 2) show a distinction between dolomites of Upper Muschelkalk and Lettenkohle (Tab. 3). Although
Lettenkohle and Upper Muschelkalk Dolomite Matrix exhibit similar crystal sizes, Lettenkohle dolomites exhibit cell parameters and %mol CaCO₃ values smaller than values obtained for the Upper Muschelkalk dolomites. Cell parameters of Upper Muschelkalk dolomites from core segment 3 yield a mean %Ca of 52.06%. Muschelkalk dolomites from core segment 4 have higher cell parameters and thus a mean %Ca of 52.68%. Lettenkohle dolomites are associated to a mean stoichiometry of 51.06%Ca. Three samples in core segment 2 with low dolomite abundances (< 7%) and poorly resolved dolomite peaks in X-ray profiles were not taken into account in the mean values of %Ca.

TABLE 3

Stoichiometry calculated on Upper Muschelkalk and Lettenkohle dolomites based on $a(=b)$ and $c$ linear regressions from this study. Three samples from Lettenkohle displaying inaccurate stoichiometry values between $a(=b)$ and $c$ equations due to low dolomite contents and not well-individualised dolomite diffraction peaks on X-ray profiles have been excluded (in grey).

Although two samples in Upper Muschelkalk also show a low dolomite content, they are characterized by a better quality dolomite X-ray profile allowing to calculate an accurate stoichiometry with both $a(=b)$ and $c$ equations.

| Sample name | Dolomite (%) | $a = b$ (Å) | $c$ (Å) | Ca (%mol) with $a(=b)$ | Ca (%mol) with $c$ | Mean %Ca $a$ and $c$ |
|-------------|--------------|-------------|---------|------------------------|-------------------|-----------------------|
| LETTENKOHLE |              |             |         |                        |                   |                       |
| 2-3 f       | 76           | 4.8087(5)   | 16.029(0) | 51.04                  | 51.47             | 51.26                 |
| 2-3 e       | 96           | 4.8080(2)   | 16.028(0) | 50.85                  | 51.42             | 51.13                 |
| 2-3 e (fracture) | 100     | 4.8089(2)   | 16.026(9) | 51.10                  | 51.37             | 51.24                 |
| 2-3 d       | 27           | 4.8081(7)   | 16.024(2) | 50.90                  | 51.23             | 51.06                 |
| 2-3 b       | 97           | 4.8077(7)   | 16.022(4) | 50.79                  | 51.13             | 50.96                 |
| 2-3 a       | 99           | 4.8088(4)   | 16.025(6) | 51.07                  | 51.32             | 51.20                 |
| 2-4 e       | 66           | 4.8077(8)   | 16.022(2) | 50.79                  | 51.13             | 50.96                 |
| 2-4 d       | 88           | 4.8091(0)   | 16.029(0) | 51.13                  | 51.47             | 51.30                 |
| 2-4 b       | 7            | 4.8145(9)   | 16.015(3) | 52.69                  | 50.78             | 51.74                 |
| 2-4 a       | 3            | 4.8237(1)   | 15.986(8) | 55.24                  | 49.41             | 52.33                 |
| 2-11 a      | 26           | 4.8096(4)   | 16.037(0) | 51.29                  | 51.86             | 51.58                 |
| 2-12 f      | 4            | 4.8116(2)   | 16.006(6) | 51.85                  | 50.39             | 51.12                 |
| 2-12 e      | 74           | 4.8057(4)   | 16.011(4) | 50.20                  | 50.59             | 50.40                 |
| 2-12 d      | 35           | 4.8069(4)   | 16.015(3) | 50.54                  | 50.78             | 50.66                 |
| 2-12 b      | 26           | 4.8077(6)   | 16.021(1) | 50.79                  | 51.08             | 50.93                 |
| Average (core 2) |         | 4.8081(2)   | 16.024(3) | 50.87                  | 51.24             | 51.06                 |
| Up. MUSCHELKALK |          |             |         |                        |                   |                       |
| 3-7 c       | 90           | 4.8083(7)   | 16.028(0) | 50.96                  | 51.42             | 51.19                 |
| 3-7 b       | 90           | 4.8092(2)   | 16.030(3) | 51.18                  | 51.52             | 51.35                 |
| 3-7 a       | 85           | 4.8125(2)   | 16.045(0) | 52.11                  | 52.25             | 52.18                 |
| 3-8 f       | 82           | 4.8118(9)   | 16.037(4) | 51.94                  | 51.86             | 51.90                 |
| 3-8 e       | 42           | 4.8105(6)   | 16.044(7) | 51.57                  | 52.25             | 51.91                 |
| 3-8 d       | 88           | 4.8115(4)   | 16.041(8) | 51.83                  | 52.11             | 51.97                 |
| 3-8 c       | 8            | 4.8142(1)   | 16.038(0) | 52.58                  | 51.91             | 52.25                 |
| 3-8 b       | 21           | 4.8124(6)   | 16.043(3) | 52.11                  | 52.16             | 52.13                 |
| 3-8 a       | 74           | 4.8123(9)   | 16.046(2) | 52.08                  | 52.30             | 52.19                 |
| 3-9 b       | 16           | 4.8145(4)   | 16.080(0) | 52.67                  | 53.97             | 53.32                 |
| 3-9 a       | 54           | 4.8129(5)   | 16.047(4) | 52.25                  | 52.35             | 52.30                 |
| Average (core 3) |         | 4.8118(8)   | 16.043(8) | 51.93                  | 52.19             | 52.06                 |
| 4-5 f       | 26           | 4.8124(5)   | 16.048(7) | 52.11                  | 52.45             | 52.28                 |
| 4-5 e       | 21           | 4.8153(9)   | 16.066(4) | 52.92                  | 53.28             | 53.10                 |
| 4-5 d       | 6            | 4.8154(8)   | 16.067(9) | 52.95                  | 53.38             | 53.16                 |
| 4-5 c       | 18           | 4.8136(0)   | 16.050(3) | 52.53                  | 52.50             | 52.51                 |
| 4-5 b       | 41           | 4.8132(3)   | 16.055(4) | 52.30                  | 52.74             | 52.52                 |
| 4-5 a       | 15           | 4.8135(7)   | 16.051(4) | 52.41                  | 52.55             | 52.48                 |
| Average (core 4) |         | 4.8139(5)   | 16.056(7) | 52.54                  | 52.82             | 52.68                 |
| AVERAGE (3 & 4) |       | 4.8126(1)   | 16.048(4) | 52.15                  | 52.41             | 52.28                 |
sedimentary rocks, the abundance of dolomite in samples is correlated to the stoichiometry (Fig. 8). When the dolomite amount increases in sediments dolomite is related to a lower %CaCO₃. However, such a trend is not as clear in the Lettenkohle samples (Fig. 8). The stoichiometry calculation for Upper Muschelkalk and Lettenkohle dolostones is robust for a wide range of dolomite abundances (Fig. 9) as the difference between the stoichiometries calculated with the \( a = b \) and \( c \) linear regressions is in general smaller than 0.6%. This difference tends to get larger only when the dolomite abundance in sample is smaller than 6% (Fig. 9). Upper Muschelkalk dolomites show higher and scattered lattice parameters \((a = b)\) values than Lettenkohle dolomites, displaying lower and less variable lattice parameters (Fig. 10). The deficiency of larger Ca ions in the unit cell of Lettenkohle dolomites compared to Upper Muschelkalk dolomites is potentially a cause for the contraction in the \( a \) direction (see Rosen et al., 1988). The expansion of the \( c \) parameter has been previously related to a cation disordering (Reeder and Wenk, 1983) or other lattice defects (Miser et al., 1987). This is an explanation for the \( c \) variability of Upper Muschelkalk dolomites and could be caused by a faster crystallization (Rosen et al., 1988) compared to Lettenkohle dolomites.

### 4.4 Dolomites and Reservoir Properties

The Upper Muschelkalk and Lettenkohle dolomites have their own properties (Tab. 4). The near-ideal stoichiometry and the small variability of the \( c \) parameter in Lettenkohle dolomites

![Figure 8](image_url)

Dolomite stoichiometry (mean value based on \( a = b \) and \( c \) linear regressions) related to the dolomite content in Upper Muschelkalk and Lettenkohle sediments. The three Lettenkohle samples linked to inaccurate stoichiometry values are not considered (see Tab. 2).

![Figure 9](image_url)

Calculated difference between the stoichiometries determined with \( a = b \) and \( c \) linear regressions depending on the dolomite content in Upper Muschelkalk and Lettenkohle sediments. The three Lettenkohle samples related to inaccurate stoichiometry values are not considered (see Tab. 2).

![Figure 10](image_url)

Unit cell dimensions of Upper Muschelkalk and Lettenkohle dolomites. The dark dashed line connects the unit cell values of calcite to magnesite. Ideal dolomites (from Rosen et al., 1989; Reeder, 1990) are situated below this line due to the unit cell contraction when dolomite is well ordered. Eugui sample from this study is also indicated. The three Lettenkohle samples associated to inaccurate stoichiometry values are not considered (see Tab. 2).
intermediate stages consisting of more disordered crystals (dolomite mineral in equilibrium with its pore fluids, including of a non stoichiometric dolomite to a pure stoichiometric sediments which differs from Upper Muschelkalk sediments. This relation might explain the pervasive matrix dolomitization in Lettenkohle mal marine settings and dolomite forms. This relation might the associated deposits may not be prominent, as it is in nor-
elevated salinity in these environments, calcite cementation of
precipitation and early dolomitization of other carbonates at low
ated with strong microbial activity, promoting dolomite pre-
shallow-water evaporative environments are associ-
ted to ideal stoichiometry through dolomitization (Fig. 8). In contrast, a sabkha model combined to a burial dolomitization are favoured for explaining Lettenkohle dolomite forma-
tion. Arguments that support the sabkha-related dolomitization are based on their near-perfect stoichiometry, their well-ordered lattice parameters and the occurrence of evaporite relicts, evidenced by nodular and displacive anhydrite (Fig. 3, 10, Tab. 3). Shallow-water evaporative environments are associated with strong microbial activity, promoting dolomite precipita-
cation and early dolomitization of other carbonates at low temperatures (Schreiber and El Tabakh, 2000). As a result of elevated salinity in these environments, calcite cementation of the associated deposits may not be prominent, as it is in normal marine settings and dolomite forms. This relation might explain the pervasive matrix dolomitization in Lettenkohle sediments which differs from Upper Muschelkalk sediments.

The dolomite recrystallization leads to the transformation of a non stoichiometric dolomite to a pure stoichiometric dolomite mineral in equilibrium with its pore fluids, including intermediate stages consisting of more disordered crystals (i.e. Ostwald ripening; Sibley et al., 1994). This process commonly generates large crystals which grow at the expense of smaller ones (Morse and Casey, 1988; Nader et al., 2004). Dolostone reservoir properties are related to their crystal size distributions, with more permeable dolostones being those consisting of overall larger crystals (Lucia, 1995). Therefore, in stable nearly stoichiometric sabkha-type dolomites, as Lettenkohle finely-crystalline dolostones, no further reser-
voir-enhancement is expected with burial and recrystallization. In contrast, reservoir properties of metastable poorly stoichiometric dolostones, originally composed of high Ca content dolomites, have the potential to improve with burial/ recrystallization. However, on a larger scale, non stoichio-
metric dolomites could dissolve in one area and reprecipitate in another causing either porosity enhancement or porosity occlusion.

**CONCLUSION**

This paper documents an approach for the stoichiometry calculation of dolomites based on using linear regressions linking the %Ca and the unit cell parameters values (a = b or c) obtained from a cell refinement on XRD profiles, also used for mineralogical quantification. Because mineral abundance and unit cell parameters determinations are not solely based on the d_{104} main dolomite diffraction peak, this approach allows quantification and stoichiometry calculation of dolomite with a better accuracy and precision relative to previous methods. The value and applicability of this method is directly demonstrated on Triassic reservoir rocks. The dolomite types from Upper Muschelkalk and Lettenkohle could be well distinguished by means of the stoichiometry calculation approach proposed in this contribution. Based on the stoichiometry level, the Upper Muschelkalk dolomites were prone to recrystallization during burial diagenesis, leading to increasing crystal sizes which potentially can enhance their reservoir quality. The originally near-
stoichiometric, very finely crystalline, sabkha dolomites of Lettenkohle were less affected by recrystallization and remained with a lower reservoir quality, although they were
subjected to the burial diagenetic environment, as Upper Muschelkalk dolomites. Stoichiometry calculation can hence help in characterizing dolomites and draws ideas concerning their reservoir potentiality.

ACKNOWLEDGMENTS

M. Joachimski, Erlangen, Germany is acknowledged for stable isotopes analyses. A. Person and UPMC Mineralogy Collection are thanked for giving access to Eugui sample. We are grateful to an anonymous reviewer for his constructive criticism of the manuscript. F. Ropital is thanked for the editorial handling of the manuscript.

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