Identification of Common Minerals Using Stoichiometric Calibration Method for Dual-Energy CT

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Abstract Medical X-ray computed tomography (CT) can be used to rapidly and non-destructively characterize structure and density variations of geological specimens. More information about the nature of samples (electron density and elemental composition) can be retrieved using multi-spectral approaches. This paper explores one of them, a stoichiometric calibration method for dual-energy imaging, to identify the most common minerals. A set of 18 calibrating materials was selected to cover a range of variability in effective atomic number ($Z_{\text{eff}}$) and electron density ($\rho_e$) encountered in geological specimens. The validation of this calibration was performed analyzing 23 common minerals by mapping their respective $Z_{\text{eff}}$ and $\rho_e$ in order to identify the one with the closest properties. This study shows that the stoichiometric method correctly identifies the most important and common minerals (quartz, calcite, dolomite) that are usually not distinguishable using a single energy imaging method, although all the 23 studied minerals were not correctly determined. We show that this method previously elaborated for medical purposes is also efficient in earth science.

Plain Language Summary Medical CT-scanners measure the attenuation of X-rays that go through a sample allowing the non-destructive 3D internal structure visualization of a wide range of samples. The attenuation depends on the interaction between incident beam and sample local density and chemical composition. By scanning specimens using two different energies, it is possible to track the attenuation changes (gray level) according to the X-ray spectra, and to use this difference to identify the samples. This paper tests the applicability of one method developed by medical physicists for biological tissues on 23 common minerals. While all minerals are not correctly identified, this method recognizes the most important and common ones in geology (quartz, calcite, dolomite).

1. Introduction

X-ray computed tomography (CT) is a non-destructive technique allowing the visualization of sample internal structure. A medical CT scanner consists in an X-ray source and a detector, which face each other and rotate around the sample. Bi-dimensional radiographic projections are acquired at various angles from 0° to 360° and then processed by a mathematical algorithm (i.e., image reconstruction) in order to obtain a 3D visualization of the object. Different types of image reconstructions exist, including the widely used filtered backprojection that requires little computational resources but produces less qualitatively accurate images, and iterative reconstruction, based on time consuming and numerically intensive algorithm but providing better images quality (Bushberg et al., 2012).

The images are displayed in a gray scale related to the X-ray attenuation by the sample materials (Rizescu et al., 2001).

Initially, this technology was developed for medical imaging, but its potential for other domains was rapidly understood (Mees et al., 2003).

This paper explores a specific CT methodology, called dual-energy CT scanning (DECT), elaborated for the first time in the seventies by Alvarez and Makovski (1976). The technique consists in imaging objects with two different X-ray spectra and in combining the results to achieve various objectives, including one allowing the discrimination and identification of materials based on their density and elemental composition. From a physical perspective, DECT exploits the energy dependence of photoelectric absorption and Compton scattering.

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components of total attenuation (Duchesne et al., 2009). The method of Alvarez and Makovski (1976) acts on the 2D radiographic projections and is therefore called a pre-reconstruction one.

During the same year, Rutherford et al. (1976) published another DECT methodology which, on the contrary, is post-reconstruction, meaning the correction is performed on the reconstructed data. This method is more sensitive to beam hardening artifacts, caused by the presence of highly attenuating materials in the sample (Remysen & Swennen, 2006). Several variations of the post-reconstruction approach have been developed afterward, in order to improve sample characterization (e.g., Jackson and Hawkes, 1981; Vinegar and Wellington, 1987; Torikoshi et al., 2003; Tsunoo et al., 2004; Bazalova et al., 2008).

One of the first DECT post-reconstruction applications in geology field was made by Van Geet et al. (2000), who adapted the mathematical formulas previously elaborated by Coenen and Maas (1994) in order to quantify the electron density ($\rho_e$) and the effective atomic number ($Z_{eff}$) of reservoir rocks, properties originally analyzed only by destructive techniques (Alves et al., 2015). Then, geologists continued to improve this post-reconstruction dual-energy method ad hoc for earth’s science (Duliu et al., 2003; Rizescu et al., 2001), sometimes building home-made CT scanner (Iovea et al., 2006; Iovea et al., 2009; Remyesn & Swennen, 2008).

Later, Pazireh et al. (2016) applied the method of Alvarez and Makovski (1976) on geological samples adopting a protocol used for medical purposes. DECT techniques typically require the knowledge of the incident X-ray beam spectrum, a feature that is not always easy to calculate or to measure (Remysen & Swennen, 2006). Therefore, DECT methods that do not require spectral information were developed and applied mostly to the field of medical imaging (e.g., Landry et al., 2013 and Bourque et al., 2014). While several authors explored the use of DECT on geological samples (e.g., Alves et al., 2015; Jussiani and Appoloni, 2015; Siddiqui and Khamees, 2004; Victor et al., 2017), they were mainly using micro-CT instruments for which the incident spectrum was easily available, focusing on artificial dense objects (metal bars) (Rezvan et al., 2011), or requiring intensive computation (Victor et al., 2017). This paper is the first to explore the use of polynomial DECT protocol to identify natural mineral samples because it has two main advantages: it can be easily be applied on medical CT images for which the spectral information of the incident X-ray is not easy to obtain or to measure, and it is computationally light.

2. Materials and Methods

2.1. CT-Scan Instrument

The instrument used in this paper is a Siemens Somatom Definition AS+128 located at the Institut national de la recherche scientifique, Centre Eau Terre Environnement, Québec City, Canada. In this configuration the gantry moves along the examination table where the samples are placed (Figure 1) (Brunelle et al., 2016).

The X-ray tube can be operated at potentials between 70 and 140 keV and the 64-row detector is from the Stellar Infinity generation. Images were acquired in spiral mode with a pitch factor of 0.55, at 70 and 140 keV, 495 mA current and a beam collimation of 12 mm. Here, the reconstruction was performed with the ADMIRE suite, belonging to the category of statistical iterative reconstruction methods (Gordic et al., 2014). Reconstructed images are $512 \times 512$ pixels, covering a field of view of $50 \times 50$ mm wide (voxels of 97 μm along the axis). Pixel values depend on the object attenuation coefficient according to Beer’s law (Cnudde & Boone, 2013), and expressed in Hounsfield units (HU), a relative scale tied to the attenuation of materials (conventionally water has $HU = 0$ and air $HU = -1000$), varying from $-1024$ to $+3071$ HU (normal scale), providing 4096 levels of gray (Brunelle et al., 2016). The CT-scale can be extended by scaling down the HU value by a factor of 10, expanding the
possible values between −10240 and 30710 HU, a feature useful for very dense samples (Coolens & Childs, 2003). The reconstruction filter used was the D45s specifically designed by Siemens for dual-energy measurements and providing a balance between the preservation of spatial resolution and noise reduction.

2.2. Stoichiometric Method

The stoichiometric method developed by Bourque et al. (2014) is a dual-energy CT protocol aiming at identifying the nature of biological tissues for medical purposes. It was based on the work of Schneider et al. (1996), a calibration elaborated for single energy CT, and Bourque et al. applied it to DECT, in order to facilitate the determination of effective atomic number \( Z_{\text{eff}} \) and electron density \( \rho_e \).

The theoretical effective atomic number \( Z_{\text{eff}} \) of samples is calculated with the following equation:

\[
Z_{\text{eff}} = \frac{\rho}{\sum_{i=1}^{N} f_i Z_i^\beta}
\]

where \( f_i \) is the fractional mass of element \( Z_i \). As the literature reports, the exponent \( \beta \) can vary between 2.94 and 3.8 (Bonnin et al., 2014; Spiers, 1946) and it is a function of photon energy, sample materials and system specifics (Alves et al., 2015; Azevedo et al., 2016; Landry et al., 2013).

Then, the theoretical electron density \( \rho_e \), expressed in number of electrons per unit volume (electron·cm\(^{-3}\)), is calculated as:

\[
\rho_e = \sum_{i=1}^{N} \frac{Z_i}{A_i} \rho
\]

where \( A_i \) is the atomic mass of the element \( Z_i \) and \( \rho \) is the material mass density (g·cm\(^{-3}\)) (Manohara et al., 2008; Azevedo et al., 2016).

The materials linear attenuation coefficient is calculated converting back CT measurements (HU values) as (Boespflug et al., 1995; Watanabe, 1999):

\[
\mu = \frac{\mu_{\text{sample}}}{\mu_{\text{water}}} = \left( \frac{\text{HU}}{1000} \right) + 1
\]

Two different calibration procedures are necessary: the first one relates to the effective atomic number and the second one to the electron density.

First, the two linear attenuation values, measured at low and high energy (Equation 3), and the calculated \( Z_{\text{eff}} \) (Equation 1) of the basis set of samples are plotted to estimate the best relationship. In our case a second-order polynomial (Equation 4) data-driven empirical model was used to set the \( a \), \( b \) and \( c \) coefficients of the \( Z_{\text{eff}} \) calibration.

\[
Z_{\text{eff}} = a + b \left( \frac{\mu_{\text{low}}}{\mu_{\text{high}}} \right) + c \left( \frac{\mu_{\text{low}}}{\mu_{\text{high}}} \right)^2
\]

It is then possible to achieve the \( \rho_e \) calibration (finding another set of coefficients) plotting the ratio between measured \( \mu \) and \( \rho_e \) (Equation 2), normalized by water electron density \( (\rho_{e\text{ water}} = 3.34 \times 10^{23}) \) and \( Z_{\text{eff}} \) determined in Equation 4:

\[
\frac{H_{\text{low at high}}}{\rho_e \rho_{e\text{ water}}} = d + e \cdot Z_{\text{eff}} + f \cdot Z_{\text{eff}}^2
\]

Again, the data-driven empirical model is a second-order polynomial. The \( \mu \) value can equally be those obtained low or high energy; it is also possible to use both equations to calculate \( \rho_e \) and average the outcomes.
3. Results

3.1. Calibration

The calibration procedure consists in scanning a set of materials with a known chemical composition (their $Z_{\text{eff}}$ and $\rho_e$ are calculated using Equations 1 and 2) in order to determine the unknown coefficients of Equations 4 and 5.

A set of 18 calibration materials covering the range of $Z_{\text{eff}}$ and $\rho_e$ encountered in geological specimens (Figure 2) was selected: common geological minerals (halite, crystalline quartz, pyrite, fluorite, albite) completed by Sodium Iodide (NaI) solutions at different concentrations, an aluminum and a titanium bar. The first ones are natural samples, so they do not have a precise chemical composition and always contain impurities, but their presence is important for the subsequent validation, being of the same nature as investigated samples (Stamm, 1974). Details about these calibration materials are available in Table S1 in Dataverse repository (see Data Availability Statement).

As anticipated, the best possible $\beta$ exponent (Equation 1) varies between 2.94 and 3.8 (Bonnin et al., 2014) depending on the material, the instrument and the energy considered. Our choice is based on the behavior of determination coefficient ($R^2$) as function of $\beta$ in the fitting of Equation 4; Figure 3 shows the best value in the possible range is 2.94.

The effective atomic number calibration, following Equation 4 to find $a$, $b$ and $c$ coefficients, is performed by plotting the $Z_{\text{eff}}$ and $\mu_{\text{low}}/\mu_{\text{high}}$ values of basis samples (Figure 4); this fit presents $R^2 = 0.97$. 

Figure 2. Electronic density and effective atomic number theoretical value distribution of calibration samples.
Figure 3. $R^2$ values against possible $\beta$ of Equation 1.

Figure 4. Coefficients related to Equation 4 and calibration curve with $\mu_{\text{low}}/\mu_{\text{high}}$ as function of $Z_{\text{eff}}$.

$$a = 31.6640$$
$$b = -41.3636$$
$$c = 20.2761$$
Then, the electron density calibration, related to Equation 5 aiming to obtain $d$, $e$ and $f$ coefficients, is shown in Figure 5. As already mentioned, we can freely choose to use $\mu_{low}$ or $\mu_{high}$ in this model. We opted for $\mu_{low}$ obtained at 70 keV because the correlation was stronger ($R^2 = 0.98$) compared to the one obtained at 140 keV ($R^2 = 0.96$).

3.2. Validation

A set of 23 relatively common minerals were used for the validation of the stoichiometric method (Table 1, column 1). Samples were about the same size as the ones of the calibration set ($\approx 3 \times 3$ cm), and selected to ensure they cover a wide range of effective atomic number and electronic density. Their theoretical values of $Z_{\text{eff}}$ and $\rho_e$ have been calculated using Equations 1 and 2 (Table 1, columns 3 and 4) starting from their theoretical chemical composition (Table 1, column 2).

Using the same acquisition conditions of the calibration step (Equation 4) the $Z_{\text{eff}}$ model and the measured linear attenuation coefficients $\mu$ (Equation 3) at low and high energy (details are available in Table S2, Dataverse repository, see Data Availability Statement), we calculate the minerals $Z_{\text{eff}}$ values (Table 1, column 5). Then, the relative difference between these measured values of $Z_{\text{eff}}$ and the theoretical ones is shown in column 6 (Table 1).

Figure 5. Coefficients related to Equation 5 and calibration curve with $Z_{\text{eff}}$ as function of $\mu_{low}/(\rho_e/\rho_e_{\text{water}})$. 

\[ d = 0.0817 \]
\[ e = 0.0383 \]
\[ f = 0.0071 \]
Table 1
Validation Minerals With Their Theoretical Chemical Composition and Theoretical $Z_{\text{eff}}$ and $\rho_e$ Calculated Using Equations 1 and 2. Then, $Z_{\text{eff}}$ and $\rho_e$ Calculated Using Stoichiometric Method and Their Relative Difference (in %) With the Theoretical Values

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Chemical composition</th>
<th>Theoretical $Z_{\text{eff}}$</th>
<th>Theoretical $\rho_e$ (e$^{-}$ cm$^{-1}$)</th>
<th>Measured $Z_{\text{eff}}$</th>
<th>Measured $\rho_e$</th>
<th>% Difference between theoretical and measured $Z_{\text{eff}}$ values</th>
<th>% Difference between theoretical and measured $\rho_e$ values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Albite</td>
<td>NaAlSi$_2$O$_5$</td>
<td>11.472</td>
<td>7.82·10$^{23}$</td>
<td>11.743</td>
<td>7.81·10$^{23}$</td>
<td>2.4%</td>
<td>0.1%</td>
</tr>
<tr>
<td>Almandine</td>
<td>Fe$_2$$^{3+}$Al$_2$SiO$_4$</td>
<td>18.655</td>
<td>1.23·10$^{24}$</td>
<td>20.514</td>
<td>9.44·10$^{23}$</td>
<td>9.9%</td>
<td>2.2%</td>
</tr>
<tr>
<td>Andesine</td>
<td>(Ca,Na)(Al,Si)$_2$O$_6$</td>
<td>13.249</td>
<td>7.97·10$^{23}$</td>
<td>12.599</td>
<td>8.32·10$^{23}$</td>
<td>3.1%</td>
<td>4.3%</td>
</tr>
<tr>
<td>Ankerite</td>
<td>Ca(Fe$^{3+}$,Mg,Mn)(CO$_3$)$_2$</td>
<td>16.989</td>
<td>9.05·10$^{23}$</td>
<td>15.094</td>
<td>7.29·10$^{23}$</td>
<td>11.2%</td>
<td>19.4%</td>
</tr>
<tr>
<td>Anorthite</td>
<td>CaAl$_2$Si$_2$O$_8$</td>
<td>13.206</td>
<td>8.21·10$^{23}$</td>
<td>12.778</td>
<td>8.27·10$^{23}$</td>
<td>3.2%</td>
<td>0.6%</td>
</tr>
<tr>
<td>Augite</td>
<td>(Ca,Mg,Fe$^{2+}$,Fe$^{3+}$,Ti,Al)$_2$(Si,Al)$_3$O$_8$</td>
<td>14.849</td>
<td>1.01·10$^{24}$</td>
<td>15.589</td>
<td>9.58·10$^{23}$</td>
<td>4.9%</td>
<td>5.6%</td>
</tr>
<tr>
<td>Biotite</td>
<td>K(Mg,Fe$^{2+}$)$_3$</td>
<td>14.046</td>
<td>9.26·10$^{23}$</td>
<td>13.741</td>
<td>7.7·10$^{23}$</td>
<td>2.2%</td>
<td>16.1%</td>
</tr>
<tr>
<td>Bytownite</td>
<td>(Ca,Na)[Al$_2$(Si,Al)$_3$O$_8$]</td>
<td>12.961</td>
<td>8.09·10$^{23}$</td>
<td>11.953</td>
<td>8.13·10$^{23}$</td>
<td>7.8%</td>
<td>0.4%</td>
</tr>
<tr>
<td>Calcite</td>
<td>CaCO$_3$</td>
<td>15.079</td>
<td>8.15·10$^{23}$</td>
<td>15.398</td>
<td>7.96·10$^{23}$</td>
<td>2.1%</td>
<td>2.3%</td>
</tr>
<tr>
<td>Chalcopyrite</td>
<td>CuFeS$_2$</td>
<td>24.568</td>
<td>1.20·10$^{24}$</td>
<td>22.741</td>
<td>9.55·10$^{23}$</td>
<td>7.4%</td>
<td>20.4%</td>
</tr>
<tr>
<td>Diopside</td>
<td>CaMg$_2$Si$_2$O$_6$</td>
<td>13.729</td>
<td>1.02·10$^{24}$</td>
<td>13.971</td>
<td>9.59·10$^{23}$</td>
<td>1.1%</td>
<td>6.1%</td>
</tr>
<tr>
<td>Dolomite</td>
<td>CaMg$_2$CO$_3$</td>
<td>13.057</td>
<td>8.53·10$^{23}$</td>
<td>13.101</td>
<td>8.46·10$^{23}$</td>
<td>0.3%</td>
<td>0.9%</td>
</tr>
<tr>
<td>Gypsum</td>
<td>CaSO$_4$2H$_2$O</td>
<td>14.109</td>
<td>7.11·10$^{23}$</td>
<td>14.246</td>
<td>7.13·10$^{23}$</td>
<td>0.9%</td>
<td>0.2%</td>
</tr>
<tr>
<td>Hematite</td>
<td>Fe$_2$O$_3$</td>
<td>22.962</td>
<td>1.52·10$^{24}$</td>
<td>17.882</td>
<td>1.73·10$^{24}$</td>
<td>22.1%</td>
<td>13.9%</td>
</tr>
<tr>
<td>Ilmenite</td>
<td>FeTiO$_3$</td>
<td>21.327</td>
<td>1.37·10$^{24}$</td>
<td>18.331</td>
<td>1.40·10$^{24}$</td>
<td>14.1%</td>
<td>2.4%</td>
</tr>
<tr>
<td>Labradorite</td>
<td>(Ca,Na)(Si,Al)$_3$O$_8$</td>
<td>16.608</td>
<td>8.06·10$^{23}$</td>
<td>12.558</td>
<td>8.26·10$^{23}$</td>
<td>0.4%</td>
<td>2.5%</td>
</tr>
<tr>
<td>Magnetite</td>
<td>Fe$_3$O$_4$</td>
<td>23.231</td>
<td>1.47·10$^{24}$</td>
<td>20.773</td>
<td>8.57·10$^{23}$</td>
<td>10.6%</td>
<td>41.9%</td>
</tr>
<tr>
<td>Microcline</td>
<td>KAlSi$_3$O$_6$</td>
<td>13.018</td>
<td>7.64·10$^{23}$</td>
<td>12.558</td>
<td>7.95·10$^{23}$</td>
<td>3.5%</td>
<td>3.9%</td>
</tr>
<tr>
<td>Muscovite</td>
<td>KAl$_2$(Si$_2$Al$_4$)(OH,F)$_3$</td>
<td>12.403</td>
<td>8.46·10$^{23}$</td>
<td>12.999</td>
<td>8.06·10$^{23}$</td>
<td>4.8%</td>
<td>4.7%</td>
</tr>
<tr>
<td>Olivine</td>
<td>(Mg,Fe)$_2$SiO$_4$</td>
<td>15.215</td>
<td>9.80·10$^{23}$</td>
<td>12.701</td>
<td>9.60·10$^{23}$</td>
<td>16.5%</td>
<td>2.1%</td>
</tr>
<tr>
<td>Phlogopite</td>
<td>K(Mg,Si$_3$Al$_4$)(F,OH)$_2$</td>
<td>12.278</td>
<td>8.46·10$^{23}$</td>
<td>14.769</td>
<td>5.43·10$^{23}$</td>
<td>20.3%</td>
<td>35.7%</td>
</tr>
<tr>
<td>Quartz</td>
<td>SiO$_2$</td>
<td>11.561</td>
<td>7.97·10$^{23}$</td>
<td>11.632</td>
<td>8.11·10$^{23}$</td>
<td>0.6%</td>
<td>1.7%</td>
</tr>
<tr>
<td>Talc</td>
<td>Mg$_5$Si$_2$O$_7$(OH)$_3$</td>
<td>11.154</td>
<td>8.30·10$^{23}$</td>
<td>11.587</td>
<td>8.52·10$^{23}$</td>
<td>3.9%</td>
<td>2.7%</td>
</tr>
</tbody>
</table>

Successively and always using the same acquisition conditions, Equation 5, the $\rho_e$ model and the measured linear attenuation coefficients $\mu$ acquired at low energy, we calculate the minerals $\rho_e$ (Table 1, column 7). Again, the relative difference between this measured values of $\rho_e$ and the theoretical ones is shown in column 8 (Table 1).

### 3.3. Mineral Identification

The next step is to develop a tool to identify unknown minerals using $Z_{\text{eff}}$ and $\rho_e$ values measured by the dual-energy stoichiometric method. An ad hoc library of 69 common minerals (chosen from the database [webmineral.com/](http://webmineral.com/), accessed Oct. 2020) was built using Python 3.7 as programming language (CommonMinerals_database.py in Dataverse repository, see Data Availability Statement) mapping them to their respective $Z_{\text{eff}}$ and $\rho_e$ (theoretically properties calculated by Equations 1 and 2).

$Z_{\text{eff}}$ and $\rho_e$ values differ by two orders of magnitude, thus they are normalized using the feature scaling method (Youn & Jeong, 2009):

$$x' = \frac{x - \min(x)}{\max(x) - \min(x)}$$
where \( x \) is the original value and \( x' \) is the normalized value. Then, another Python routine (Minerals_Identification.py in Dataverse repository, see Data Availability Statement) searches this library to find the minerals with the shortest Euclidean distance to these theoretical properties, and provides a list of minerals with increasing Euclidean distance.

Table 2 shows the three closest minerals found using the searching program for each validation set of samples from Table 1.

### 4. Discussion

The calibration step yielded very high \( R^2 \) correlation coefficients (0.97 for \( Z_{\text{eff}} \) model and 0.98 for \( \rho_e \) model), in spite of two outliers. Titanium bar in Figures 4 and 8% NaI in Figure 5 do not perfectly fit: considering similar samples perform very well (another pure metal bar and other solutes), it is difficult to explain why these two outliers appear. However, despite their presence, the calibration is adequately performed.

The stoichiometric method validation estimated the effective atomic number \( Z_{\text{eff}} \) with less than 10% difference compared to theoretical value: out of a total of 23 minerals, 17 have less than 5% difference and, conversely, the largest deviations are for magnetite, ankerite, ilmenite, olivine, phlogopite and hematite in ascending order (Table 1).

Bourque et al. (2014) obtained a smaller error, but in this study 10% is acceptable considering the samples we investigated, denser and more complex than human tissues; moreover, the final goal is the mineral identification among those of a chosen database, which is influenced by several factors and not only by the percentage error.
Figure 6 shows the iterative reweighted least squares trendline (red line) of minerals theoretical versus measured $Z_{\text{eff}}$ perfectly matches with the least squares trendline (black line) and the theoretical trendline (dashed line, slope = 1); comparing the slopes, we observe our measurements underestimates the values.

The results for electron density $\rho_e$ characterization are similar: 16 minerals have a difference between the measured and the theoretical values of less than 10%, of which 14 of them less than 5%, and the largest difference occurs for hematite, biotite, ankerite, chalcopyrite, almandine, phlogopite and magnetite in ascending order (Table 1).

Figure 7 shows that iterative reweighted least squares trendline (red line) of minerals theoretical versus measured $\rho_e$ involves a clear improvement of the fit compared to the least square method (black line), perfectly matching with the theoretical dashed line (slope = 1); nevertheless most outliers present underestimated values.

The identification routine allowed to correctly pinpoint 7 minerals, including very common ones, i.e., albite, quartz and calcite (Table 2). An interesting example is hematite: its identification is well performed, although its properties values present an high percentage error. Considering $Z_{\text{eff}}$ and $\rho_e$ distribution of the 69-mineral library (Figure 8), we observe the majority is situated in a cluster of the graph having small $Z_{\text{eff}}$ and $\rho_e$ instead, common minerals with high $Z_{\text{eff}}$ and $\rho_e$ are less frequent. Thus, we successfully identified hematite even though its validation performance is weak because the Euclidean distance to its closest neighbor is larger than others (Figure 8).
Several reasons could explain why some mineral samples have a wide difference between theoretical and measured values. First, because natural minerals contain impurities that are unknown in this experiment, it is likely the $Z_{\text{eff}}$ and $\rho_e$ calculated using Equations 1 and 2 and theoretical mineral compositions are not reflecting the actual composition of the minerals used for both the calibration and the validation.

The second reason, similar to the first one, is that some minerals can easily interchange cations within their lattice, yet their precise elemental composition is rather impossible to obtain without specific analysis. Nine validation minerals fall under this case, explaining the poor identification obtained for phyllosilicates, such phlogopite, muscovite and biotite, and others such as ankerite (Table 1). However, chalcopyrite, hematite, ilmenite and magnetite, in spite of their chemical formula not allowing for lattice cation substitutions, also have large differences with theoretical results for $Z_{\text{eff}}$, $\rho_e$, or both properties: these minerals are the densest ones and, among the validation samples, it is remarkable that their values are mainly underestimated, according to iterative least squares trend. The performance of the stoichiometric protocol, previously developed for medical physics and human tissues, could be weaker for dense samples. It is possible that the exposure time with our medical CT is too low for having an accurate measurement of $\mu$. Figure 9 shows the cross plot of minerals $\mu$ at low and high energy and the relative error bars having 95% confidence level: it is calculated following (Hazra, 2017):

$$x \pm Z \frac{s}{\sqrt{n}}$$

where $x$ is our measurement, $Z$ is the value for determining confidence interval (here $Z = 1.96$), $s$ is the standard deviation and $n$ is the number of observations.
In order to avoid the overlapping, only some samples are illustrated but all of them present the same characteristic: horizontal error bar, related to low energy, is larger than the vertical one. This is true for minerals having large or small confidence intervals, so, probably, the need for improving the signal-to-noise ratio is stronger for lower voltage acquisitions (Gordic et al., 2014).

The third possible reason is this stoichiometric method is not so well suited for dense samples; indeed, Bourque et al. used 140 keV as high energy, but the materials they aimed to characterize have smaller values of $Z_{\text{eff}}$ and $\rho_e$ than those investigated here. However, this explanation does not hold a close examination of our results because some dense minerals such as hematite and ilmenite (Z$_{\text{eff}}$ = 22.96 and 21.3 respectively) are correctly identified (Table 2). Our probable explanation is the answer resides in a combination of the above-mentioned factors: some samples have an underestimation for $Z_{\text{eff}}$ and an overestimation for $\rho_e$ and inversely, bringing the minerals in a value range favorable to their identification. Indeed, having a small relative difference between theoretical and measured values is not always sufficient to correctly identify the objects using the shortest Euclidean distance.

A possible improvement of this stoichiometric method could reside in increasing the exposure time or to acquire repeated scans in order to improve the signal-to-noise ratio (e.g., Larmagnat et al., 2019), especially when very dense minerals, reducing the number of photons reaching the detectors, are present.

While the list of existing minerals totals more than 4000, our ad hoc library was limited to the 69 most common ones; however, in the most of the cases, some basic knowledge of natural samples such a rock would considerably shorten the list of potential minerals, hence improving the rate of correct classification. If the list of dense potential minerals remains limited to one or two, the method will likely be able to provide a correct identification.
Therefore, despite some drawbacks, stoichiometric method is a suitable option for the characterization of important and common minerals for geological field (quartz, calcite, dolomite) that are not distinguishable using single energy imaging method having very similar density values. Because CT-scanning rock and sediment cores is fast and non-destructive, this method is laying the foundation for an easy access to mineralogical information on geological samples.

5. Conclusion

Stoichiometric calibration is a methodology previously elaborated for medical purposes aiming to characterize the human tissues while removing the need for the knowledge of the incident X-ray energy spectra.

This work tested for the first time this technique on geological specimens, materials of greater density than the formerly studied biological samples. Two different calibrations were performed to characterize the effective atomic number and the electron density using six natural minerals, two metal bars and 11 saline solutions at different concentrations. Then, the calibration was validated with a set of 23 natural mineral samples selected to ensure they cover a wide range property values. Finally, an ad hoc routine search the minerals closest to the calculated \( Z_{\text{eff}} \) and \( \rho_e \) values and provides a list of decreasing possibilities.

We showed this stoichiometric dual-energy CT method is easy to implement and well suited to identify the most common minerals.

Data Availability Statement

All the data about calibration materials, measured linear attenuation coefficients \( \mu \) of minerals and the Python scripts used for their identification are available at the Dataverse repository: https://doi.org/10.5683/SP2/P4IY8Y.

Figure 9. Cross plot of minerals \( \mu \) at low and high energy and the relative error bars having 95% confidence level.
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