

Oxygen Isotopic Fractionation in the Kaolinite-Water System during the Synthetic Process

E. Caballero*, C. Jiménez de Cisneros

Instituto Andaluz de Ciencias de la Tierra (UGR-CSIC), Armilla, Spain

Email: *emilia.caballero@csic.es

How to cite this paper: Caballero, E. and Jiménez de Cisneros, C. (2018) Oxygen Isotopic Fractionation in the Kaolinite-Water System during the Synthetic Process. *Journal of Minerals and Materials Characterization and Engineering*, 6, 507-516.
<https://doi.org/10.4236/jmmce.2018.64036>

Received: June 19, 2018

Accepted: July 28, 2018

Published: July 31, 2018

Copyright © 2018 by authors and Scientific Research Publishing Inc. This work is licensed under the Creative Commons Attribution International License (CC BY 4.0).

<http://creativecommons.org/licenses/by/4.0/>



Open Access

Abstract

Oxygen isotope fractionation is studied during the synthesis of kaolinite under controlled conditions of temperature and time. Equilibrium conditions have been established and its relationship with temperature has been studied. Kaolinite was hydrothermally precipitated starting from non-crystalline aluminosilicate gels. The amount of kaolinite obtained increases up to a limited constant value and in all cases coexists with the amorphous starting gels. It can be seen that the data obtained at 48 hours of synthesis can be considered as quasi-equilibrium, since the total isotopic equilibrium has not been reached, only the sample obtained at 24 hours should be discarded for studies in equilibrium. This would allow us, with the samples obtained at 720 hours, to try to establish a relationship between isotopic fractionation and temperature, provided that we know the water in equilibrium with the synthesized kaolinite. Two equations have been obtained that show correlation coefficients with a high statistical significance.

Keywords

Oxygen Isotopic Fractionation, Kaolinite-Water System, Isotopic Equilibrium

1. Introduction

Isotopic composition measurements on natural or synthetic systems can be used to establish quantitative relationships between isotopic composition and temperature of the system [1] [2] [3] [4]. Isotopic composition of clay minerals is thus a function of the temperature of formation and of the $^{18}\text{O}/^{16}\text{O}$ ratio of the ambient water. As long as the oxygen isotopic composition acquired by a clay mineral at the time of its formation remains unaltered, it can provide information con-

cerning the nature of the environment in which the mineral formed. Equilibrium hydrogen and oxygen isotopic fractionations between clay minerals and water have been reviewed by [4] [5] and [6], among others.

The fractionations between clay minerals and water are commonly estimated using several approaches: 1) laboratory equilibrium experiments [7]; 2) naturally occurring samples; 3) statistical mechanical calculations [8] [9] [10] [11] [12]; 4) empirical calculations [13]. Each approach has its advantages and disadvantages.

Laboratory equilibration techniques have been summarized by [14]. When it is possible to demonstrate that isotopic equilibrium has been reached between the mineral and water, laboratory equilibrium studies provide the most accurate estimates of isotopic fractionation factors. However, slow rates of isotopic exchange generally preclude the attainment of sufficiently large amounts of oxygen isotopic exchange between clay minerals and water below 200°C and hydrogen isotope exchange below 100°C. Thus, this approach is not suitable for the estimation of equilibrium fractionations between clays and water under pedogenic conditions.

Statistical mechanical methods for calculating isotopic fractionation factors has been described and summary [14]. There have been few published attempts to calculate fractionation factors for clay-water systems. However, the results [8] suggest that this method is useful for obtaining oxygen isotope fractionation factors at low temperatures between minerals and water. Given the lack of accurately determined isotopic fractionation factors for clay minerals, empirical or semiempirical approaches may be used. In one approach, the bond-type method, assume that oxygen in a chemical bond has similar isotopic behavior regardless of the mineral in which the bond is located [5] [15] [16]. These calculations are limited by the accuracy with which fractionations between individual oxygen-containing bonds and water are known, and by the fact that the assumption underlying the method is not strictly accurate. However, comparisons of the results of this technique with the few experimentally determined fractionation factors at surficial temperatures give reasonable agreements. The method has the advantage of permitting an estimate of the effects of variable chemical composition of minerals like smectite on the isotopic behaviour of the minerals.

Empirical methods determine isotopic fractionation factor from the isotopic composition of natural samples. To use this method it must be assumed that the isotopic composition of the formation water is known and that the mineral has been formed in isotopic equilibrium. Another empirical approach that may prove useful in estimating oxygen isotope fractionations of clays formed under surface and near-surface conditions, is the increment method [17] as modified by [18] [19].

On the other hand, synthesis mineral reaction could be a useful method to study the fractionation factors in equilibrium-disequilibrium isotopic between mineral-water at controlled conditions, because in this case a completely new chemical (mineral) is formed and regardless of the isotopic composition of the water, equilibrium is approached from only one direction. That is, equilibrium

may be attained during the reaction (and generally is at temperatures higher than about 550°C), but it difficult to be proved. [14] says that synthesis is not fruitful line of approach that it would appear to be and results of such experiments, particularly if performed at low temperatures, are viewed with considerable skepticism.

The aim of this paper is to study the oxygen fractionation factors in the kaolinite-water system during the experimental synthesis of this mineral at different temperatures. This approach may be interesting because we could know the most accurate estimates of isotopic fractionation factors at low temperatures.

2. Materials and Methods

2.1. Starting Material

Starting materials were prepared according to the procedure described by [20]. Amorphous aluminosilicates (Si/Al atomic ratios 1.84, 1.54, 1.26, 0.99, 0.84 and 0.76) were precipitated by co-hydrolysis of tetraethyl orthosilicate and aluminium tri-isopropoxide (Merck reagents), dried at 60°C and ground.

Patterns of X-ray powder diffraction (XRD) (Philips PW 1730; graphite monochromed CuK α radiation) show only a very wide band centred at 3.5 - 4 Å (Figure 1). No crystalline phases were detected.

Differential thermal analysis and thermogravimetry (DTA-TG) were carried out using a Netzsch simultaneous thermal apparatus (STA 409 PE). Specific surface area was measured by the water adsorption method (Keeling, 1961), ranged from 434 to 778 m²·g⁻¹. Chemical analysis were performed by X-Ray fluorescence spectrometry (XRF; Philips PW1404) on pressed powder pellets.

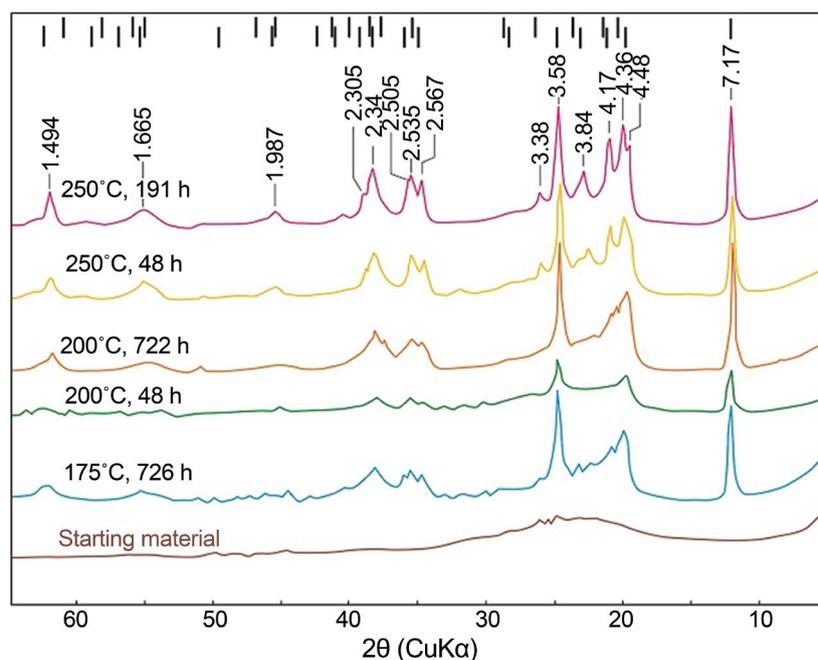


Figure 1. DRX pattern for the starting gel together with the samples of kaolinite obtained at different times and temperatures from [19].

2.2. Hydrothermal Treatment

The gels (2.5 g) were hydrothermally aged in KOH 0.1 M solution (10 ml), in Teflon-lined reactors, by heating in an oven at the pre-fixed temperatures (150°C, 175°C, 200°C, 225°C and 250°C). The pressure inside the reactors was at the corresponding water vapour pressure: 4.7, 8.8, 15.3, 25.2 and 39.8 atm, respectively. The aging times varied from 6h up to 60 days. More details about the synthesis method are given in [20] and [21].

2.3. Characterization of Synthetics Products

The solid precipitated were characterized by surface area, XRD and DTA-TG analyses following the same procedures as those described for the starting material and had been published by [21]. Kaolinite was the only crystalline phase found in the products of the runs and its formation and crystallinity depended on time, temperature, and Si/Al ratio of the starting material. Qualitative chemical analysis and morphological observations was carried out by SEM-EDX and had been published by [22].

Oxygen isotopic compositions of the solids were determined by the method [23]. After the removal of interlayer water by heating at 200°C for 8hour under vacuum, the oxygen was extracted from the clay minerals by fluorination. It was then purified and converted to CO₂ using a vacuum line. Isotope analyses of the samples studied show a standard deviation of replicate $\delta^{18}\text{O}$ -values less than $\pm 0.2\%$. All values reported are relative to VSMOW. CO₂ was measured in a Finnigan Mat 251 mass spectrometer with VSMOW as standard reference and analytical precision of $\pm 0.1\%$. Oxygen isotopic composition of the starting water were determined by equilibrium between CO₂ and H₂O at 25°C, in accord by [24] method.

Oxygen isotopic fractionation has been done in 10 synthetic samples from two different starting gels (MK-7 and MK-10) at temperatures indicated before and at 720 hours. The study of the precipitation kinetics has been carried out by determining the fractionation factor as a function of time, in a series of samples obtained at 200°C from MK10 starting gel.

3. Results and Discussion

XRD diagrams realised in the solids shows kaolinite as the only crystalline phase found in the products of the runs, as well as amorphous aluminosilicates that is changing gradually in kaolinite when temperature increase. Products synthesized at higher temperature contain more kaolinite which was more crystalline than in the experiments carried out at lower temperatures [21]. Because the several experiences were carried out in a closed systems the production of kaolinite decrease when the aluminosilicate gels decrease. The amount of kaolinite obtained increase up to a limited constant value and in all cases kaolinite coexists with the amorphous gels. **Figure 1** shows DRX pattern for the starting gel together with the samples of kaolinite obtained at different times and temperatures

from [21].

Isotopic fractionation values for synthesized samples from the MK10 gel, as well as the isotope exchange (%), the reaction times and temperature, are shown in **Table 1**. It is observed that for the same temperature (200°C), the isotopic fractionation value ($\alpha_{\text{kaolinite}}$) tends to increase as a function of time, except for the sample synthesized at 24 hours, because the amount of solid synthesized at this time has been so small that the isotopic value obtained, is very similar to that of the starting gel. If we observe the value of starting gel (12.1‰) it is only different with that of the sample in a 0.7‰.

The determination of isotope exchange % was performed according to [14], for which the value of isotopic fractionation factor for water at the end of each experiment was estimated by mass balance:

$$\text{isotope exchange (\%)} = \left(\frac{\Delta_i - \Delta_f}{\Delta_i} \right) * 100$$

$$\Delta_i = \delta^{18}O_i - \delta^{18}O_{wi} = 1000 \ln \alpha_i$$

$$\Delta_f = \delta^{18}O_f - \delta^{18}O_{wf} = 1000 \ln \alpha_f$$

The rate of oxygen isotopic exchange in experimental exchange processes is near to zero at temperatures below 300°C unless chemical or mineralogical changes occur [25]. Clays are extremely resistant to post-formational isotopic exchange at surficial temperatures in the absence of chemical or mineralogical reaction. At higher temperatures (>100°C) small but measurable amounts of oxygen and hydrogen isotopic exchange between clays and water occur on a laboratory time scale. There is evidence that hydrogen isotopes exchange more rapidly than oxygen isotopes [25].

During a synthesis process, isotopic fractionation occurs because chemical and mineralogical changes occur, even when the reaction time and the temperature are low. This does not imply that at the end of each experiment the kaolinite solid (gel + kaolinite) is in equilibrium with the solution, although what [14] calls a “True equilibrium” or “quasi-equilibrium” state could be achieved. On

Table 1. Isotopic fractionation values for synthesized samples from MK10 gel, as well as isotope exchange (%) and reaction times at 200°C. $\Delta_i = \delta^{18}O_i - \delta^{18}O_{wi} = 1000 \ln \alpha_i$; $\Delta_f = \delta^{18}O_f - \delta^{18}O_{wf} = 1000 \ln \alpha_f$.

Sample	Time (hours)	$\alpha_{\text{kaolinite}}$	α_{gel}	α_{water}^i	α_{water}^f	Δ_i	Δ_f	Isotope exchange (%)
K129	24	1.01143	1.0121	0.9918	0.99247	20.46	18.92	6.6
K123	48	1.00440	1.0121	0.9918	0.99949	20.46	4.91	76
K71	96	1.00485	1.0121	0.9918	0.99905	20.46	5.79	71.7
K72	191	1.00500	1.0121	0.9918	0.99890	20.46	6.09	70.2
K73	361	1.00538	1.0121	0.9918	0.99852	20.46	6.85	66.5
K54	720	1.00567	1.0121	0.9918	0.99823	20.46	7.42	63.3

the other hand, in a synthesis experiment, kinetic isotope effects are possible and rigorous proof of equilibrium is usually lacking. However, the study of [26] on oxygen isotope fractionations between water and feldspar have demonstrated that simple exchange and synthesis experiments involving cation exchange can give concordant fractionations. Similarly, they showed that cation exchange reactions and synthesis of muscovite from gels also gave concordant results [27].

In **Table 1** it is verified that sample synthesized at 48 hours, shows an isotopic exchange value higher than 75%. The samples synthesized at higher time shows an isotope exchange percentage with an average value of 67.72%. This indicates that the system has not reached equilibrium but the values obtained are high enough to be considered as “quasi-equilibrium” or “true-equilibrium”.

The isotope exchange decrease by increasing the time of synthesis, would be in agreement with [14], that in experiments of experimental isotopic exchange of quartz in aqueous medium at 500°C observes that the rates of isotopic exchange are relatively high at the beginning of the process, because are controlled by surface exchange, and then become progressively lower with time to be controlled by diffusion processes.

“Rates of isotopic exchange reactions in heterogeneous systems are relatively high at first (surface controlled) and then become progressively lower with time (diffusion controlled)”.

Relationship between Isotope Fractionation and Temperature

Table 2 shows the selected samples from MK7 and MK10 starting gels for the study of isotopic fractionation as a function of temperature. The time in all cases has been 720 hours. The oxygen isotopic exchange has been determined and we can observe that at 200°C the values are close to 100%. The value at 150°C shows lower isotopic exchange and has therefore been discarded for this study. In **Table 2** is also possible to observe how the value of the isotopic fractionation of the synthesized samples decreases with the temperature, according to the established in the principles of isotope geochemistry.

Although the values obtained for isotope fractionation show systems outside the isotopic equilibrium, values higher than 60% of isotopic exchange are considered of “quasi-equilibrium”. This has led us to try to establish the relationship between the isotopic fractionation and temperature using the values obtained at 720 hours.

The oxygen isotopic fractionation between kaolinite and water ($1000 \ln \alpha_{\text{kaolinite-water}}^{18}$) in function of the synthesis temperature for the samples of the two starting gels considered, can be expressed from the equations:

$$\text{MK10: } 1000 \ln \alpha_{\text{kaolinite-agua}}^{18} = 1203.10^6 T^{-2} - 44.42 \quad (R^2 = 0.941)$$

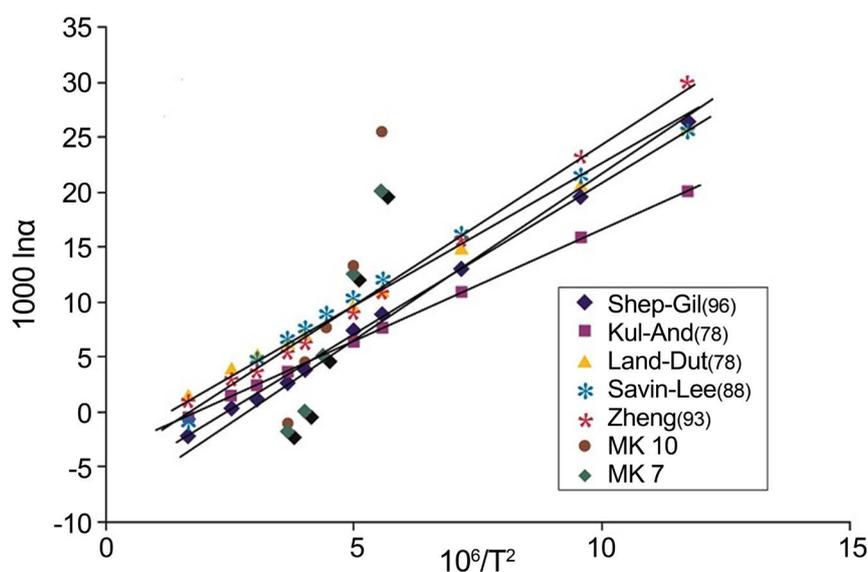
$$\text{MK7: } 1000 \ln \alpha_{\text{kaolinite-agua}}^{18} = 1055.10^6 T^{-2} - 39.96 \quad (R^2 = 0.9303)$$

Both equations have correlation coefficients with a high statistical significance.

Figure 2 shows both lines of oxygen isotopic fractionation for MK10 and MK7 together with the lines of oxygen isotopic fractionation as a function of

Table 2. Selected samples from MK7 and MK10 starting gels for the study of isotopic fractionation as a function of temperature at 720 hours.

Starting gel	Sample	Temp. (°C)	$\alpha_{\text{kaolinite}}$	α_{gel}	α_{water}^i	α_{water}^f	Isotope exchange (%)	$1000 \ln \alpha$
MK10								
	K52	150	1.01464	1.0121	0.9918	0.98926	25.02	25.43
	K53	175	1.00823	1.0121	0.9918	0.99567	38.2	12.64
	K54	200	1.00567	1.0121	0.9918	0.99823	63.3	7.52
	K55	225	1.00416	1.0121	0.9918	0.99974	78.2	4.51
	K154	250	1.00133	1.0121	0.9918	1.00257	106	1.14
MK7								
	K40	150	1.0167	1.0213	0.9918	0.9964	31.2	20.27
	K41	175	1.0128	1.0213	0.9918	1.0003	57.6	12.52
	K42	200	1.0092	1.0213	0.9918	1.0039	82.03	5.37
	K43	225	1.0066	1.0213	0.9918	1.0065	99.7	0.198
	K148	250	1.0057	1.0213	0.9918	1.0074	105	1.59

**Figure 2.** Oxygen isotopic fractionation lines for kaolinite-water system obtained by different methods, together with lines obtained in this study (MK-7 and MK10).

temperature that appear in the literature obtained by different methods. Thus the equations of [5] and [19] are theoretical. The equation obtained by [28] uses the empirical method; and the semi-empirical method has been used by [4]. Experimental method is used by [29]. All these equations are determined on the basis of isotopic equilibrium in the kaolinite-water system. In our system the equilibrium has not been totally reached, so the slope of the line obtained in our case is different from those obtained by the rest of the authors. Only the values

determined at temperatures of 175 °C and 200 °C are similar to the equilibrium equations.

It should be noted that the solid obtained is not 100% kaolinite but contains different contents of the starting gel, this may cause the value of the isotopic fractionation obtained to be not the real one but will be influenced by the different chemical composition of the different solids according to [14] [29].

4. Conclusions

The study of the oxygen isotopic fractionation in kaolinite-water system from the synthesis of this mineral leads us to affirm that for the experimental conditions (720 hours and 200 °C), the final kaolinitic solid obtained has not reached the isotopic equilibrium with the solution, although samples synthesized at longer times show a percentage of isotopic exchange with an average value close to 70%. This indicates that the system has not reached equilibrium but the values obtained are high enough to be considered as “quasi-equilibrium” state.

The equations obtained for $1000 \ln \alpha_{\text{kaolinite-water}}^{18}$ for the samples synthesized from the two starting gels: MK7 and MK10, show correlation coefficients with a high statistical significance. However the slope of the lines obtained are different of those obtained by other authors because the solid obtained is not 100% kaolinite and have different contents of the starting gel.

If the amount of kaolinitic solid had been close to 100% and no starting gel residue remained, the slope of the equations obtained would probably resemble more closely other equations described in the literature. In future works and improving the synthesis system we will obtain Kaolinites in which the isotopic equilibrium is reached and not “True equilibrium” or “quasi-equilibrium”.

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

References

- [1] Clayton, R.N. (1972) Oxygen Isotope Exchange between Quartz and Water. *Journal of Geophysical Research*, **77**, 3057. <https://doi.org/10.1029/JB077i017p03057>
- [2] Kulla, J.B. and Anderson, T.F. (1978) Experimental Oxygen Isotope Fractionation between Kaolinite and Water. In: Zartman, R.E., Ed., *Short Papers Of the 4th Int. Con., Geochronology, Cosmochronolgy, Isotope Geology, USGS, Open File Report No. 78-70*, 234-235.
- [3] Kita, I., Taguchi, S. and Matsubaya, O. (1985) Oxygen Isotope Fractionation between Amorphous Silica and Water at 34 °C - 93 °C. *Nature*, **314**, 83-84. <https://doi.org/10.1038/314083a0>
- [4] Sheppard, S.M.F. and Gilg, H.A. (1996) Stable-Isotope Geochemistry of Clay-Minerals. *Clay Mineral*, **31**, 1-24. <https://doi.org/10.1180/claymin.1996.031.1.01>
- [5] Savin, S.M. and Lee, M. (1988) Isotopic Studies of Phyllosilicates. In: Bailey, S.W., Ed., *Hydrous Phyllosilicates*, Reviews in Mineralogy Vol. 19, Mineralogical Society

- of America, Washington DC, 189-223.
- [6] Savin, S.M. and Hsieh, J.C.C. (1998) The Hydrogen and Oxygen Isotope Geochemistry of Pedogenic Clay Minerals: Principles and Theoretical Background. *Geoderma*, **82**, 227-253. [https://doi.org/10.1016/S0016-7061\(97\)00103-1](https://doi.org/10.1016/S0016-7061(97)00103-1)
- [7] Kulla, J.B. (1979) Oxygen and Hydrogen Isotope Fractionation Factors Determined in Experimental Clay-Water System. Ph.D. Thesis, Univ. Illinois at Urbana-Champaign, USA.
- [8] Kieffer, S.W. (1982) Thermodynamics and Lattice Vibrations of Minerals: 5. Applications to Phase Equilibria, Isotopic Fractionation, and High Pressure Thermodynamic Properties. *Reviews of Geophysics and Space Physics*, **20**, 827-849. <https://doi.org/10.1029/RG020i004p00827>
- [9] Clayton, R.N. and Kieffer, S.W. (1991) Oxygen Isotopic Thermometer Calibrations. In: Taylor Jr., H.P., O'Neil J.R. and Kaplan, I.R., Eds., *Stable Isotope Geochemistry: A Tribute to Samuel Epstein*, The Geochemical Society, Spec. Pub. No. 3, S. Antonio, 3-10.
- [10] Méheut, M., Lazzeri, M., Balan, E. and Mauri, F. (2007) Equilibrium Isotopic Fractionation in the Kaolinite, Quartz, Water System: Prediction from First-Principles Density-Functional Theory. *Geochimica et Cosmochimica Acta*, **71**, 3170-3181. <https://doi.org/10.1016/j.gca.2007.04.012>
- [11] Méheut, M., Lazzeri, M., Balan, E. and Mauri, F. (2010) First-Principles Calculation of H/D Isotopic Fractionation between Hydrous Minerals and Water. *Geochimica et Cosmochimica Acta*, **74**, 3874-3882. <https://doi.org/10.1016/j.gca.2010.04.020>
- [12] Meheut, M. and Schauble, E.A. (2014) Silicon Isotope Fractionation in Silicate Minerals: Insights from First-Principles Models of Phyllosilicates, Albite and Pyrope. *Geochimica et Cosmochimica Acta*, **134**, 137-154. <https://doi.org/10.1016/j.gca.2014.02.014>
- [13] Lambert, S.J. and Epstein, S. (1980) Stable Isotope Investigations of an Active Geothermal System in Valles Caldera, Jemez Mountains, New Mexico. *Journal of Volcanology and Geothermal Research*, **8**, 111-129.
- [14] O'Neil, J.R. (1986) Theoretical and Experimental Aspects of Isotopic Fractionation. Stable Isotopes in High Temperature Geologic Process. In: *Reviews in Mineralogy*, Vol. 16, 1-40.
- [15] Taylor Jr., H.P. and Epstein, S. (1962) Relationship between $^{18}\text{O}/^{16}\text{O}$ Ratios in Coexisting Minerals of Igneous and Metamorphic Rocks, Part 1. Principles and Experimental Results. *Bulletin of the Geological Society of America*, **73**, 461-480. [https://doi.org/10.1130/0016-7606\(1962\)73\[461:RBORIC\]2.0.CO;2](https://doi.org/10.1130/0016-7606(1962)73[461:RBORIC]2.0.CO;2)
- [16] Caballero, E. and Jiménez de Cisneros, C. (2010) Stable Oxygen and Hydrogen Isotopic Composition of Bentonites from Cabo de Gata (Almería, Spain). *Chemie der Erde—Geochemistry*, **70**, 69-76. <https://doi.org/10.1016/j.chemer.2009.11.001>
- [17] Schütze, V.H. (1980) Der Isotopenindex-eine Inkrementenmethode zur näherungsweise Berechnung von Isotopenaustauschgleichgewichten zwischen kristallinen Substanzen. *Chemie der Erde*, **39**, 321-334.
- [18] Zheng, Y.F. (1991) Calculation of Oxygen Isotope Fractionation in Metal-Oxide. *Geochimica et Cosmochimica Acta*, **55**, 2299-2307. [https://doi.org/10.1016/0016-7037\(91\)90105-E](https://doi.org/10.1016/0016-7037(91)90105-E)
- [19] Zeng, Y.F. (1993) Calculation of Oxygen-Isotope Fractionation in Hydroxyl-Bearing Silicates. *Earth and Planetary Science Letters*, **120**, 247-263. [https://doi.org/10.1016/0012-821X\(93\)90243-3](https://doi.org/10.1016/0012-821X(93)90243-3)

- [20] Huertas, F.J., Huertas, F. and Linares, J. (1993) Hydrothermal Synthesis of Kaolinite: Method and Characterization of Synthetic Materials. *Applied Clay Science*, **7**, 345-356. [https://doi.org/10.1016/0169-1317\(93\)90001-H](https://doi.org/10.1016/0169-1317(93)90001-H)
- [21] Huertas, F.J., Fiore, S., Huertas, F. and Linares, J. (1999) Experimental Study of the Hydrothermal Formation of Kaolinite. *Chemical Geology*, **156**, 171-190. [https://doi.org/10.1016/S0009-2541\(98\)00180-6](https://doi.org/10.1016/S0009-2541(98)00180-6)
- [22] Fiore, S., Huertas, F.J., Huertas, F. and Linares, J. (1995) Morphology of Kaolinite Crystals Synthesized under Hydrothermal Conditions. *Clays and Clay Minerals*, **43**, 353-360. <https://doi.org/10.1346/CCMN.1995.0430310>
- [23] Bortwith, J. and Harmon, R. (1982) A Note Regarding F₃Cl as an Alternative to F₅Br for Oxygen Isotope Analysis. *Geochimica et Cosmochimica Acta*, **46**, 1665-1668. [https://doi.org/10.1016/0016-7037\(82\)90321-0](https://doi.org/10.1016/0016-7037(82)90321-0)
- [24] Epstein, E. and Mayeda, T.K. (1958) Variation of the ¹⁸O/¹⁶O Ratio in Natural Waters. *Geochimica et Cosmochimica Acta*, **4**, 213-224. [https://doi.org/10.1016/0016-7037\(53\)90051-9](https://doi.org/10.1016/0016-7037(53)90051-9)
- [25] O'Neil, J.R. and Kharaka, Y.K. (1976) Hydrogen and Oxygen Isotope Exchange Reactions between Clay Minerals and Waters. *Geochimica et Cosmochimica Acta*, **40**, 241-246. [https://doi.org/10.1016/0016-7037\(76\)90181-2](https://doi.org/10.1016/0016-7037(76)90181-2)
- [26] O'Neil, J.R. and Taylor, H.P. (1967) The Oxygen Isotope and Cation Exchange Chemistry of Feldspar. *American Mineralogist*, **52**, 1414-1437.
- [27] O'Neil, J.R. and Taylor, H.P. (1969) Oxygen Isotope Equilibrium between Muscovite and Water. *Journal of Geophysical Research*, **74**, 6012-6022. <https://doi.org/10.1029/JB074i025p06012>
- [28] Land, L.S. and Dutton, S.P. (1978) Cementation of a Pennsylvanian Deltaic Sandstone: Isotopic Data. *Journal of Sedimentary Petrology*, **48**, 1167-1176.
- [29] Caballero, E. (1989) Fraccionamiento isotópico. Efecto de la composición química. *Estudios Geológicos*, **45**, 299-314. <https://doi.org/10.3989/egcol.89455-6502>