Hydrogen-Deuterium Exchange Experiments Between Laboratory Water and Clays (Pure Metahalloysite)

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Abstract: Reliability of hydrogen isotopes analyses have been discussed by some authors. Using highly depleted water all agree that the hydroxyl group in 10 Å halloysite can exchange hydrogen by 30% in minutes with interlayer water and therefore exchange is fast enough to occur during clay separation in the laboratory with ambient water. Even if most halloysite 10 Å samples were exchangeable there has not been many experiments done on collapsed 7Å halloysite (metahalloysite) because of it's re-expandable capacity. Since little information is known about halloysite-hydrogen exchange, exchange experiments were designed between laboratory water of δD-66 and -184‰ V-SMOW and clay minerals (pure metahalloysite) from two size fractions of <0.5 and 2-5 µm for 2 years at room temperature with ratio 15 mg water for 1 mg of clay were designed to prove the validity of δD.These experiments attest that metahalloysite does not allow hydrogen exchange in laboratory conditions. Therefore δD values are reliable, increases with smaller size fraction and the difference between metahalloysite and kaolinite are either related to temperature variation from 15 to 25°C or exchanges.

Key words: Metahalloysite, clay, stable isotopes, exchange experiments

INTRODUCTION

Experimental works on isotope exchange discussed by Lawrance[1-3] were performed on kaolin from Djebel Debbagh (northeastern algeria) . The kaolin ore has three different colours and textures that are composed of high-grade 99 to 90% of white kaolin (sample: F14-F18) .

Some high-grade, clay separates of pure metahalloysite that have reproducible δD values at 48±5%, (sample F18 <5 µm, '4 measurements'). Whereas most high-grade kaolin separates have quiet a scatter in δD values ranging from -to -51‰ and H_2O yields between 14.1 and 15.7 Wt.%. These yields are variable as compare to theoretical water content and might be link to metahalloysite defects or shape retaining OH.

Hydrogen for isotopic analysis was extracted from <5 µm clay-size fractions. Samples were dried at room temperature with ambient moisture at δD value of -195‰, under vacuum in quartz tube overnight at 150°C. Hydroxyl-hydrogen is liberated by complete fusion at ca. 1300°C using a butane-oxygen torch[4]. The liberated H_2O and H_2, H_2S etc is passed over a Cu oxide trap at 575°C and then converted to H_2 by reduction with uranium at 800°C)[5]. The H_2 is trapped in a sample container with activated charcoal at liquid nitrogen temperature.

MATERIELS AND METHODS

Clay separates were obtained by settling and centrifuging using distilled water with known stable-isotope values to constrain and estimate the isotopic-changes of the interlayer-water during sample purifications. The different size fractions of clays varying from <0.5, 0.5 to 1, 1 to 2, 2 to 5 µm and their relative proportions were measured by weight. The mineralogy of clay separates have been analysed using XRD, IR infrared spectroscopy and SEM techniques, to identify minerals and textures. Clay separates was determined using XRD with random and oriented sample preparations. Samples were air-dried and glycolated data were collected using a Brucker D5000 (Cu $K\alpha_{1-2}$; 2 to 65 °2 θ range) and treatment using formamide [$HCONH_2$][6,7] to re-expand interlayer from 7 to 10 Å. Infra Red (IR) spectroscopy, with clay separates, was performed on a Nicolet 510 (FTIR) on random pellets. Pellets were made with a ratio of 1 mg sample with 150 mg of KBr at room temperature and then

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oven dried at 110°C for 24 h. Infrared patterns were collected in an air-dried cell, in order to discriminate kaolinite from halloysite and metahalloysite.

These petrographical, mineralogical and chemical (H_2O weight %) results are used to determine sample purity prior to stable isotopes analyses.

Isotopic analyses of H_2 were made by conventional isotope ratio mass spectrometry using an ISOPRIME at Jean Monnet University (France). All δD values are reported in per mil (‰) relative to the Vienna-Standard Mean Ocean Water (V-SMOW). External error and reproducibility for standards and replicates for δD ±3‰ (2σ) for hydrogen extraction procedures for stable isotopes measurements

RESULTS AND DISCUSSION

XRD patterns and Infrared absorption patterns: The XRD patterns of both random and oriented samples from low to medium grade ore show mixtures of dominant kaolin with illite and illite/smectite (samples F16 and F15) interlayer
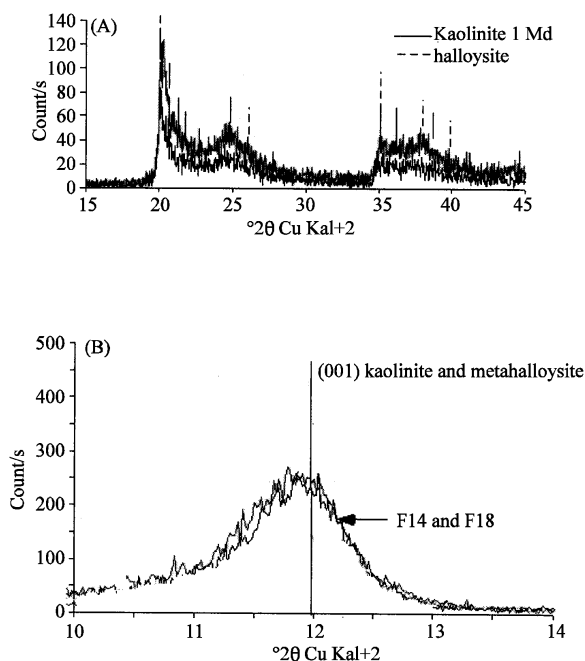

Fig. 1: A) XRD patterns (Cu Kα $_{1-2}$; from 15 to 45 °2θ range) carried out from air-dried bulk materials coming from low and high-grade kaolin ore on unoriented clay separates. B) Oriented XRD patterns (Cu Kα $_{1-2}$; from 2 to 15 °2θ range) of air-dried <0.5μm size fractions from sample F14, F 16, F18, with (hkl) peaks of alunite, 1Md-kaolinite or halloysite are, respectively shown as plain and dash lines.
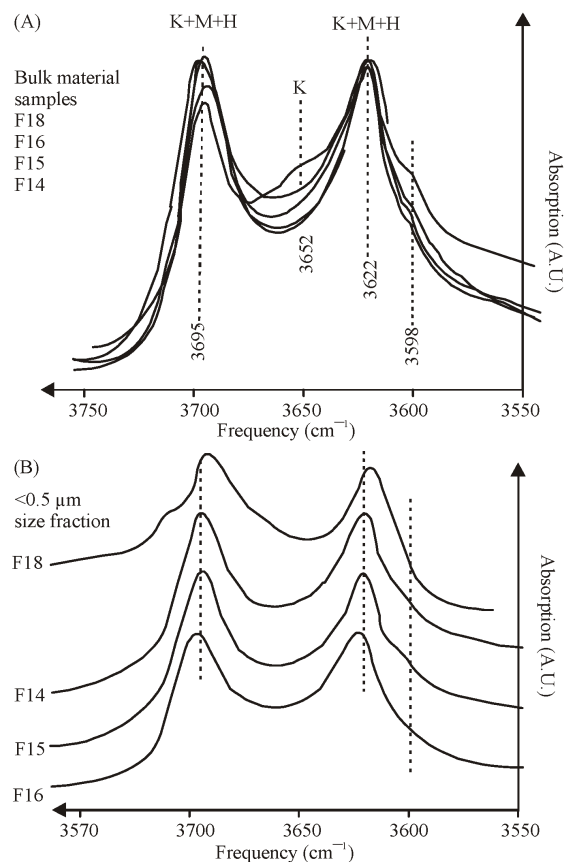

Fig. 2: Infrared absorption patterns from 3550 to 3750 cm⁻¹ carried out on air-dried samples 18, 16, 15 and 14 (A: bulk material, B: size fractions lower than 0.5 μm, samples F 18, F16, F15 and F 14). Major adsorption frequency bands are noted as dash lines with K, H and M standing for characteristic bands of kaolinite, halloysite and metahalloysite

phase (R1) with a ferruginous cap-rock. Preserved illite/smectite R1 mixed-layered clays suggest that regional temperature would have to be close to 100°C[8]. The high grade kaolin has only (hkl) peaks that could be related to 7 Å (metahalloysite) and/or 1Md kaolinite, with full widths at half height (001) ranging from 0.7 to 0.4° 2 θ for the different size fractions. Fig. 1 and none of the formamide treatment re-expand the interlayer to 10 Å.

Infrared absorption patterns of different clay-size fraction and low to high grade kaolin, reveal the presence of kaolinite and metahalloysite[9]. metahalloysite (7 Å) (Fig. 2) with inner OH-stretching bands at 3695 and 3622 cm⁻¹ and minor outer OH-stretching at 3602 and a bump at 3574 cm⁻¹. Whereas clayey three distinct bands at 3695, 3652 and 3622 cm⁻¹ often related to disordered or ordered kaolinite.

Table 1: Hydrogen-deuterium exchange experiments between lab water of δD -66 and -184‰ V-SMOW and pure metahalloysite from two size fractions of <0.5 and 2-5 μm for 2 years at room temperature with ratio 15 mg water for 1 mg of clay. Samples are then freeze-dried and step heated at a rate of 100°C per step and at 800°C fused. For each step, water amounts are normalised to total sample weight and expressed as weight % of H₂O and δD (‰ V-SMOW), total weight %, δD total and δD total above 200°C

	(δD lab water -66‰ VSMOW)		(δD lab standard -184‰ VSMOW)	
	Water/clay ratios	;15/1		;15/1
F 18 (5 to 2 μm)	weight	107.4 mg	107.2 mg	
initial temparature (°C)	Weight %	δD ‰ V-SMOW	Weight %	δD ‰ V-SMOW
ambiant-100	0.00	below detection limit	0.1	-54
100 to 200	0.45	-59	0.28	-44
200 to 300	0.52	-62	0.46	-51
300 to 400	1.60	-46	1.61	-53
400 to 500	6.13	-35	4.59	-37
500 to 600	5.28	-37	5.55	-40
600 to 700	0.00	below detection limit	1.88	-39
700 to 800	0.25	-72	0.54	-54
800 to fusion	0.13	-85	0.02	below detection limit
	δD water final = -66‰		δD water final = -175‰	
sum (ambiant to fusion) =	14.37	-42	15.02	-43
sum (200 to fusion)	13.92	-41	14.63	-43
F18 (<0.5 μm)	weight	105.4 mg	106.5 mg	
temparature (°C)	Weight %	δD ‰ V-SMOW	Weight %	δD ‰ V-SMOW
ambiant-100	0.06	-110	0.2	-44
100 to 200	0.26	-80	0.24	-38
200 to 300	0.41	-76	0.36	-35
300 to 400	0.50	-66	1.08	-44
400 to 500	1.01	-67	3.32	-52
500 to 600	3.78	-50	7.95	-43
600 to 700	6.61	-49	1.39	-57
700 to 800	1.95	-47	0.41	-72
800 to fusion	0.78	-75	0.04	below detection limit
	δD water final = -64‰		δD water final = -176‰	
sum =	15.38	-55	14.99	-47
sum (200 to fusion)	15.06	-55	14.55	-48
F14 (5 to 2 μm)	weight	101.9 mg	102.8 mg	
temparature (°C)	Weight %	δD ‰ V-SMOW	Weight %	δD ‰ V-SMOW
ambiant-100	0.21	-95	0.1	-93
100 to 200	0.25	-73	0.29	-25
200 to 300	0.3	-65	0.37	-51
300 to 400	0.6	-56	0.68	-45
400 to 500	1.79	-43	2.67	-33
500 to 600	5.74	-36	6.77	-26
600 to 700	4.44	-36	3.68	-22
700 to 800	2.2	-41	0.458	-46
800 to fusion	0.01	below detection limit	0.24	-62
	δD water final = -66‰		δD water final = -175‰	
sum =	15.52	-41	15.25	-30
sum (200 to fusion)	15.08	-40	14.86	-31
F14 (<0.5 μm)	weight	44.4 mg	50.1 mg	
temparature (°C)	Weight %	δD ‰ V-SMOW	Weight %	δD ‰ V-SMOW
ambiant-100	0.13	-133	0.02	below detection limit
100 to 200	0.41	-79	0.28	-67
200 to 300	0.45	-85	0.35	-79
300 to 400	1.10	-64	0.85	-67
400 to 500	7.23	-31	4.55	-38
500 to 600	5.77	-34	7.49	-33
600 to 700	0.54	-60	0.86	-49
700 to 800	0.22	-57	0.21	-71
800 to fusion	0.03	below detection limit	0.06	below detection limit
	δD water final = -65‰		δD water final = -174‰	
sum =	15.89	-41	14.67	-41
sum (200 to fusion	15.35	-40	14.38	-41

Hydrogen results from pure metahalloysite (samples 14 and 18 clay fractions: 5-2 and <0.5 μm) after the exchange experiments: To compare total extraction and exchange experiments for both settings, weight % of H₂O was calculated after 200°C step, subtracting adsorbed-water, from 200°C to fusion. Each experiment gave slightly different results compare to the fusion Table 1 and Fig. 3a. However, patterns of water release are similar for
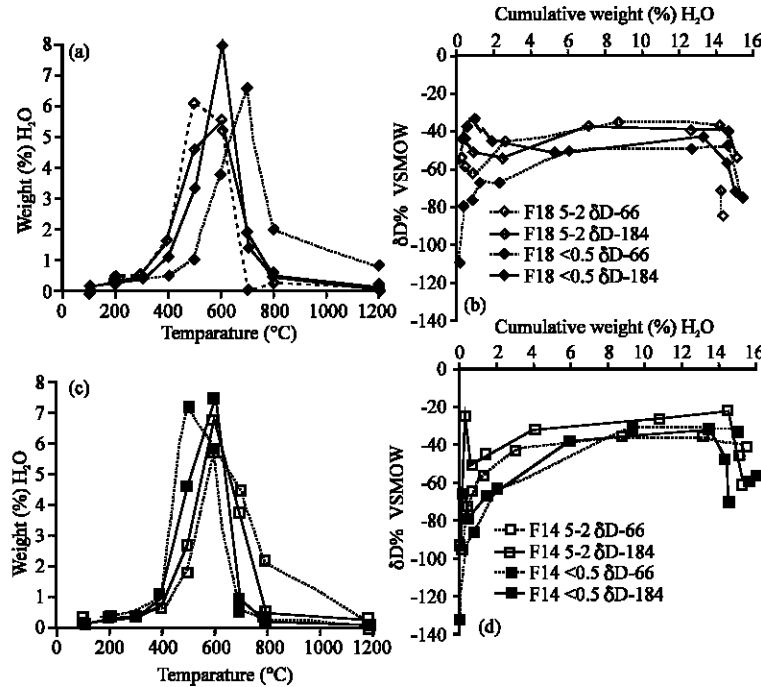
Fig. 3: Hydrogen exchange experiment are shown as (a and c) Weight % H_2O extracted vs. Temperature to distinguish adsorbed water from structural water (hydroxyl group) and (b and d) cumulative weight % H_2O vs. δD to characterize main plateau shape without isotopic composition

all experiments. The difference between these two calculations are between -0.2 to -0.6 Wt. % H_2O Table 1.

Most of the water has been extracted between 400 and 700°C with a maximum between 400 and 600°C. Out of sample 14 (5-2 μm), 90% of the water was released between 200 and 600°C. However some yields are higher, with no relation with any specific step, as in samples 14 and 18 (-184‰) of size fraction 5 to 2 μm. Weight % of H_2O are still higher than theoretical yields but doesn't seem to be related to structural shape of metahalloysite probably due to H located at defect sites with non-exchangeable capacity.

Exchanged samples (cumulative weight % H_2O vs. δD; Fig. 3b) with different δD initial water have similar patterns from low to high temperature steps. There seems to be no relation between size fractions and initial δD steps. Indeed those within water $\delta D_{initial}$: -66‰, have lower initial values than the one in $\delta D_{initial}$: -184‰. Probably related to the time of pumping, those were pumped overnight for the first. Whereas the others were for several days due to the visible moisture. However, even if most low δD fluids were removed, $\delta \Delta$ values from 0 to 300°C steps, are related to adsorbed-water with lower δD values especially for samples reacting in δD of -184‰ (initial-water). At higher temperature-steps, H_2O weight % yields measured are related to remains of adsorbed-water

and structural bonded hydroxyls. They show a progressive plateau shape of δD values between -30 and -60‰ values. From 700°C to fusion, the amount of H_2 is decreasing and δD value gets lower probably related to residual Al(O-OH) and mullite-type structure and faster hydrogen fractionation between extracting and residual hydroxyls.

Weighted-calculations from 200°C to fusion temperatures, of -66 and -184‰ exchange experiments, give in both studies δD-values slightly higher (±10‰ max) than total fusion (Table 1). However, these ±10‰ changes are not significant considering an error-propagation of ±8‰ on each step from 200°C to fusion.

Hydrogen results on water after the exchange experiments: After the exchange experiments, 99.5 weight % of water was recovered and the remainder represents adsorbed water on clays. The δD values for these recovered waters are equal to initial water (-66 to -64‰ V-SMOW; $\delta D_{initial}$: -66‰), or +8 to +10‰ heavier than $\delta D_{initial}$: -184‰ V-SMOW Table 1. This value of -184‰ δD_{water} might be due exchange or to a light water bond attached to interlayer water. δD values from pur metahalloysite after the exchange experiments were compared to hydrogen results on air-dried samples. Each experiment gave slightly different results wt. % H_2O and

δD values compare to the air-dried metahalloysite (Table 1 and Fig 3a). The δD values are ±10‰ V-SMOW and -0.2 to -0.6 wt. % H_2O between air dried samples (150°C-200°C to fusion) and exchange experiments steps (200°C to fusion, Table 1). However, these ±10‰ changes are not significant considering an estimated error of ±8‰ on each step from 200°C to fusion. Patterns of water release are similar for all experiments (Fig. 3a). Most of the water was extracted between 400 and 700°C with a maximum between 400°C and 600°C in agreement with the literature and TGA under He or N_2 atmosphere[10].

However, weight % of H_2O air-dried and exchange experiments are still up to 2% higher than theoretical yields with no relation to any specific step. Theoretical weight % of H_2O should be obtained for dehydration at 400°C which is unrealistic to remove adsorbed water. Such a high yield has to be related to defect sites with bonded-hydroxyl groups. Some samples have lighter δD values for initial step from ambient to 100°C. Higher heating-steps gave heavier and variable $δD_{metahalloysite}$ values. δD values show a progressive "plateau shape" of δD between -30 and -60‰ V-SMOW. From 700°C to fusion, the amount of H_2 decreased with the lower δD values probably related to residual Al(O-OH), mullite-type structure and faster hydrogen fractionation between extracting and residual hydroxyls. Exchanged samples (cumulative weight % H_2O vs. δD; Fig. 3b) with different $δD_{initial}$ water have similar patterns from low to high temperature steps. There seems to be no relation between size fractions and initial δD steps. These results especially with -184‰ V-SMOW labelled water do not agree with the exchange experiments realised by[11,3], which show 35% of exchange on halloysite at 25°C and predicted $δD_{metahalloysite}$ value of -110‰ V-SMOW after a few minutes. Our results emphasize that exchange of hydrogen did not occur during sample collection or lab treatment over 24 months.

CONCLUSION

In both study exchange experiments attest that metahalloysite does not allow hydrogen exchange in laboratory conditions. Therefore δD values are reliable, increases with smaller size fraction and the difference between metahalloysite and kaolinite are either related to temperature variation from 15 to 25°C or exchanges. Exchange experiments attest that metahalloysite does not allow hydrogen exchange. Therefore δD values are reliable increases with smaller size fraction and the difference between metahalloysite and kaolinite is +10 to + 20 pour mill are either related to temperature from 15 to 25°C or fluid/rock ration changes.

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