Canadian Mineralogist
Vol. 31. pp. 173-183 (1993)

PALYGORSKITE FROM FRACTURE ZONES IN THE EYE – DASHWA LAKES GRANITIC PLUTON, ATIKOKAN, ONTARIO

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Abstract

The mode of occurrence, X-ray, chemical, uranium series and stable isotope characteristics of palygorskite found in fracture zones to a depth of 25 m in the Eye–Dashwa Lakes granitic pluton, located near Atikokan, Ontario, are documented. The palygorskite formed as a product of alteration of epidote according to the reaction: epidote + chlorite + water → palygorskite + goethite ± smectite-group mineral. The palygorskite has *d* values of 10.48 to 2.28 Å, is orthorhombic (*Pbmn*), and is compositionally uniform, with cation values of Si 4.07 to 4.15, Mg 0.62 to 0.68 and Al 1.05 to 1.17, based on 11 atoms of oxygen, and minor Fe, Ca and K contents. There are significant abundances of Sr (557 μg/g), U (10 μg/g) and Th (20 μg/g), inherited from the parent epidote. U is preferentially incorporated into palygorskite, whereas Th is incorporated into goethite. It is fractionated in light rare-earth elements ($\Sigma LREE$ = 1974; La_N/Yb_N = 142) inherited from the parental epidote ($\Sigma LREE$ = 2844; La_N/Yb_N = 56). Most of the analyzed samples of palygorskite from greater depths have $^{234}U/^{238}U$ ratios close to unity, indicating secular equilibrium, whereas palygorskite samples located closer to the surface have $^{230}Th/^{234}U$ ratios greater than one, suggesting geochemical disturbance in recent times (<0.35 Ma). Stable isotope characteristics (δD between –75 and –28‰, $\delta^{18}O$ between 18.4 and 23.4‰) indicate that palygorskite formed in equilibrium with modern groundwaters at temperatures ≤ 25°C, but in some cases, it experienced selective depletion in D accompanied by loss of U.

Keywords: clay minerals, palygorskite, U-series isotopes, stable isotopes, fracture zones, plutonic rocks, water–rock interaction, Atikokan, Ontario.

Sommaire

Nous documentons ici la présence de la palygorskite jusqu'à une profondeur de 25 m dans les zones fissurées du pluton granitique des lacs Eye et Dashwa, près de Atikokan, en Ontario, ainsi que ses attributs structuraux (diffraction X), compositionnels et isotopiques (série de l'uranium et isotopes stables). La palygorskite s'est formée aux dépens de l'épidote selon la réaction: épidote + chlorite + H_2O → palygorskite + goéthite ± minéral du groupe de la smectite. Les valeurs de *d* s'échelonnent entre 10.48 et 2.28 Å. La palygorskite a une symétrie orthorhombique (*Pbmn*) et une composition homogène, contenant entre 4.07 et 4.15 atomes de Si, entre 0.62 et 0.68 atomes de Mg, et entre 1.05 et 1.17 atomes de Al par unité formulaire de 11 atomes d'oxygène; le Fe, Ca et K sont aussi présents en quantités moindres. Le strontium (557 μg/g), l'uranium (10 μg/g) et le thorium (20 μg/g) ont été hérités de l'épidote. L'uranium est incorporé préférentiellement dans la palygorskite, tandis que le Th est piégé par la goéthite. Les terres rares légères sont enrichies dans la palygorskite (concentration totale 1974 ppm; La_N/Yb_N = 142), et sont héritées de l'épidote précurseur (2844 ppm; La_N/Yb_N = 56). La plupart des échantillons analysés des zones plus profondes possèdent un rapport $^{234}U/^{238}U$ voisin de l'unité, indication d'un état d'équilibre séculaire, tandis que les échantillons de palygorskite situés plus près de la surface possèdent un rapport $^{230}Th/^{234}U$ supérieur à un, indication d'une remobilisation géochimique récente (<0.35 Ma). D'après les rapports d'isotopes stables (δD entre –75 et –128 ‰, $\delta^{18}O$ entre 18.4 et 23.4 ‰), la palygorskite se serait formée en équilibre avec de l'eau souterraine en temps modernes à une température de 25°C ou moins, avec, dans certains cas, une perte sélective en D et en uranium.

(Traduit par la Rédaction)

Mots-clés: argiles, palygorskite, isotopes de la série de l'uranium, isotopes stables, zones de fractures, roches plutoniques, interaction roche–eau, Atikokan, Ontario.

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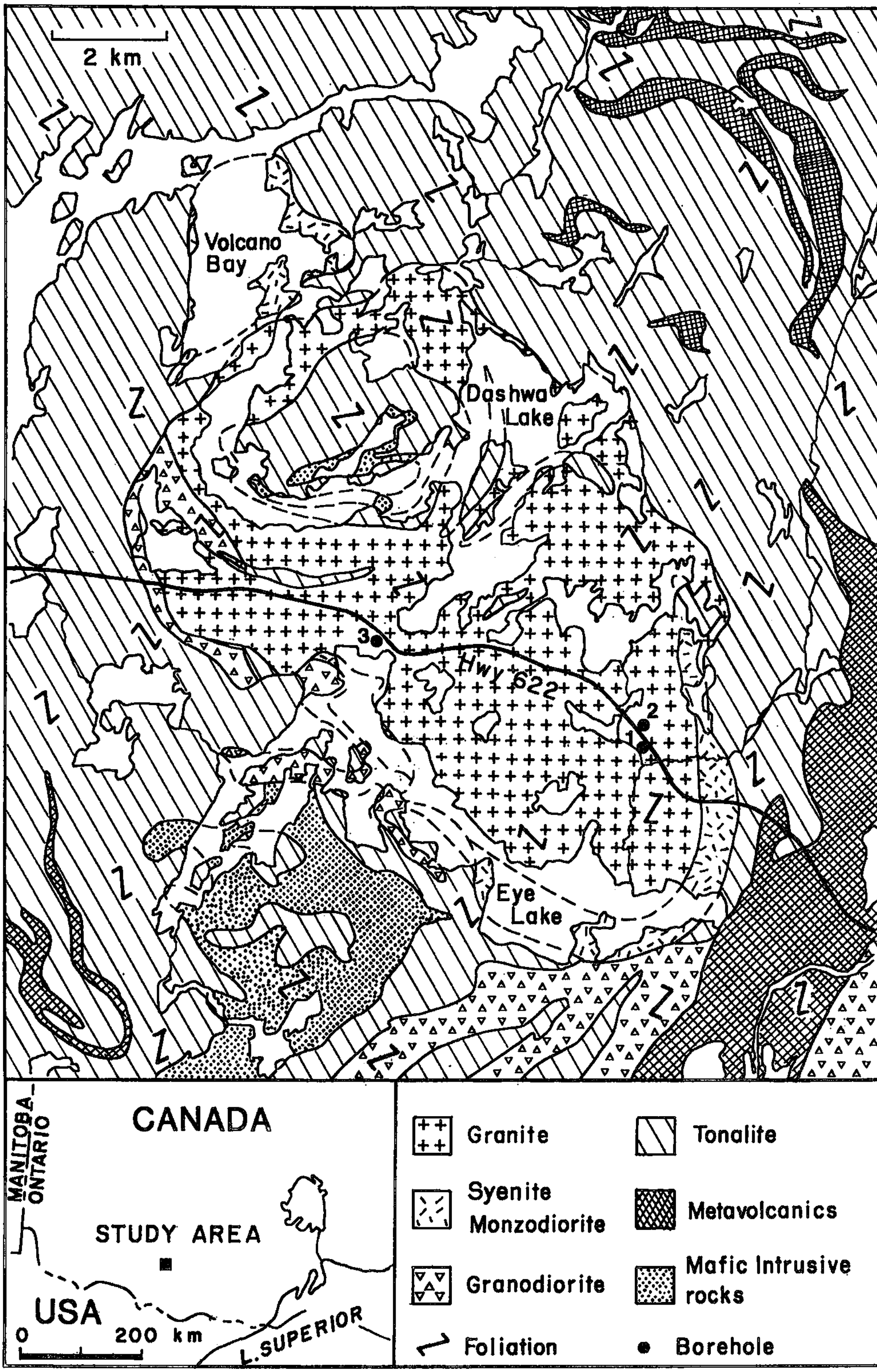
2 km
Volcano Bay
Dashwa Lake
Hwy 622
Eye Lake
1
2
3
CANADA
MANITOBA
ONTARIO
STUDY AREA
USA
0 200 km
L. SUPERIOR
Granite
Tonalite
Syenite Monzodiorite
Metavolcanics
Granodiorite
Mafic Intrusive rocks
Foliation
Borehole

INTRODUCTION

The formation of palygorskite has been reported previously in a restricted number of geological environments, including marginal marine basins, lagoons under warm climatic conditions and deep-sea occurrences (Bonatti & Joensuu 1968, Couture 1977, Weaver & Beck 1977, Weaver 1984, Millot 1970, Isphording 1973, 1984). The characteristics of palygorskite first identified in fracture zones within a granitic pluton by Kamineni (1986) are reported here; it is the only such occurrence in this environment known to the authors.

In this paper we report the mode of occurrence, X-ray-diffraction data, chemical composition, and U-series and stable isotope characteristics of the fracture-controlled palygorskite. We also discuss the genesis of palygorskite in this environment, and the attendant low-temperature water–rock interaction and migration of U, Th and daughter isotopes in fracture zones in these granitic rocks.

GEOLOGY AND MODE OF OCCURRENCE

The Eye–Dashwa Lakes granitic pluton, located about 30 km northwest of Atikokan, Ontario, occurs in the Wabigoon Subprovince of the Canadian Shield (Fig. 1). The pluton has been investigated by AECL Research as part of its research program to assess a concept for the permanent disposal of high-level nuclear fuel waste. In this context, eight cored diamond-drill boreholes ranging in depth from ~ 150 to >1200 m were drilled in order to evaluate the properties of granite at depths up to 1 km. A number of studies, on the themes of rock alteration, fracture-filling, fluid-infiltration history and fracture chronology, have been conducted on these core samples (Kamineni & Dugal 1982, Kamineni & Stone 1983, Kerrich & Kamineni 1988).

The Eye–Dashwa Lakes pluton is zoned, with a quartz monzodioritic rim and a granodioritic to granite core (Kamineni & Brown 1981). Recently, Zartman & Kwak (1990) reported the pluton's age to be 2665 Ma, based on U–Pb concordia of zircon separates. The pluton is transected by a series of fractures that are generally filled or coated with minerals (Kamineni *et al.* 1980). On the basis of the type of mineral infillings, the fractures have been divided into four groups (Stone & Kamineni 1982): (a) granite-filled fractures (pegmatites and aplites), (b) epidote-filled fractures, (c) chlorite-filled fractures, and (d) low-temperature mineral-filled fractures. Among these groups, the epidote-filled type is the most abundant, and some segments of these may contain low-temperature clay minerals, such as palygorskite. According to Kamineni *et al.* (1990), the majority of epidote-filled fractures formed at ~2300 Ma, whereas the clay replacement of epidote is likely to have been very recent (≤1 Ma: Kerrich & Kamineni 1988).

Flaky aggregates of palygorskite were found to occur as an alteration product (<1 mm thick) on pre-existing epidote-lined fractures within the Eye–Dashwa Lakes pluton. Various degrees of alteration, ranging from incipient to complete alteration of epidote, were visually noted on numerous outcrops. Palygorskite occurs in both steep- (41 to 90°) and low- to intermediate-dip (<11 to 40°) fracture zones. Although the epidote-lined fracture zones extend to depths exceeding 1 km, palygorskite is confined only to shallow regions (<100 m) and is predominant in the top 50 m, indicating that it is a product of the interaction of rock (epidote fracture-filling) and shallow groundwater. Where palygorskite-bearing fractures are exposed along steep sections in road cuts, they generally discharge water, suggesting relatively high hydraulic permeability.

SAMPLES, X-RAY DIFFRACTION AND SEM STUDIES

Flakes of palygorskite were scraped from epidote-bearing fractures exposed in outcrops located on rock cuts along Highway 622; sample locations are given in Figure 1. The palygorskite samples were collected on outcrops within 1 to 2 weeks after the rock cuts were blasted, prior to highway construction. Hence, they are considered as fresh as subsurface samples. Considerable care was exercised to eliminate rock matrix and parent material (epidote). Goethite is generally present in the

TABLE 1. CHEMICAL COMPOSITION OF PALYGORSKITE

Sample No.	1	2	3	4	5	6
Depth (m)	25.0	23.5	8.3	6.5	2.0	1.0
SiO_2 WT%	58.70	61.61	59.55	60.66	62.30	61.85
TiO_2	0.14	0.17	0.15	0.11	0.11	0.10
Al_2O_3	13.00	13.20	14.35	14.22	14.66	14.80
Fe_2O_3T	3.50	3.40	3.60	2.62	1.50	1.22
MnO	0.02	0.02	0.02	0.01	0.01	0.01
MgO	6.35	6.13	6.18	6.75	6.59	6.80
CaO	2.04	1.66	1.50	1.80	1.59	1.60
K_2O	2.22	2.47	2.11	1.85	1.90	1.55
Na_2O	0.00	0.00	0.00	0.00	0.00	0.00
P_2O_5	0.41	0.56	0.55	0.60	0.53	0.52
H_2OT	13.55	10.42	11.88	11.30	10.58	11.40
Total	99.93	99.64	99.89	99.92	99.77	99.85
Number of cations on the basis of 11 oxygens						
Si	4.10	4.15	4.07	4.10	4.15	4.14
Al	1.07	1.05	1.16	1.13	1.15	1.17
Fe^{3+}	0.18	0.17	0.19	0.13	0.08	0.06
Mg	0.66	0.62	0.63	0.68	0.65	0.68
Ca	0.15	0.12	0.11	0.13	0.11	0.11
K	0.20	0.21	0.18	0.16	0.16	0.13

Total Fe expressed as Fe_2O_3; all samples contain <0.1% CO_2

FIG. 1. Geological setting of the Eye–Dashwa Lakes pluton; 1 represents location of samples 5 and 6; 2 represents location of samples 3 and 4, and 3 represents location of samples 1 and 2.

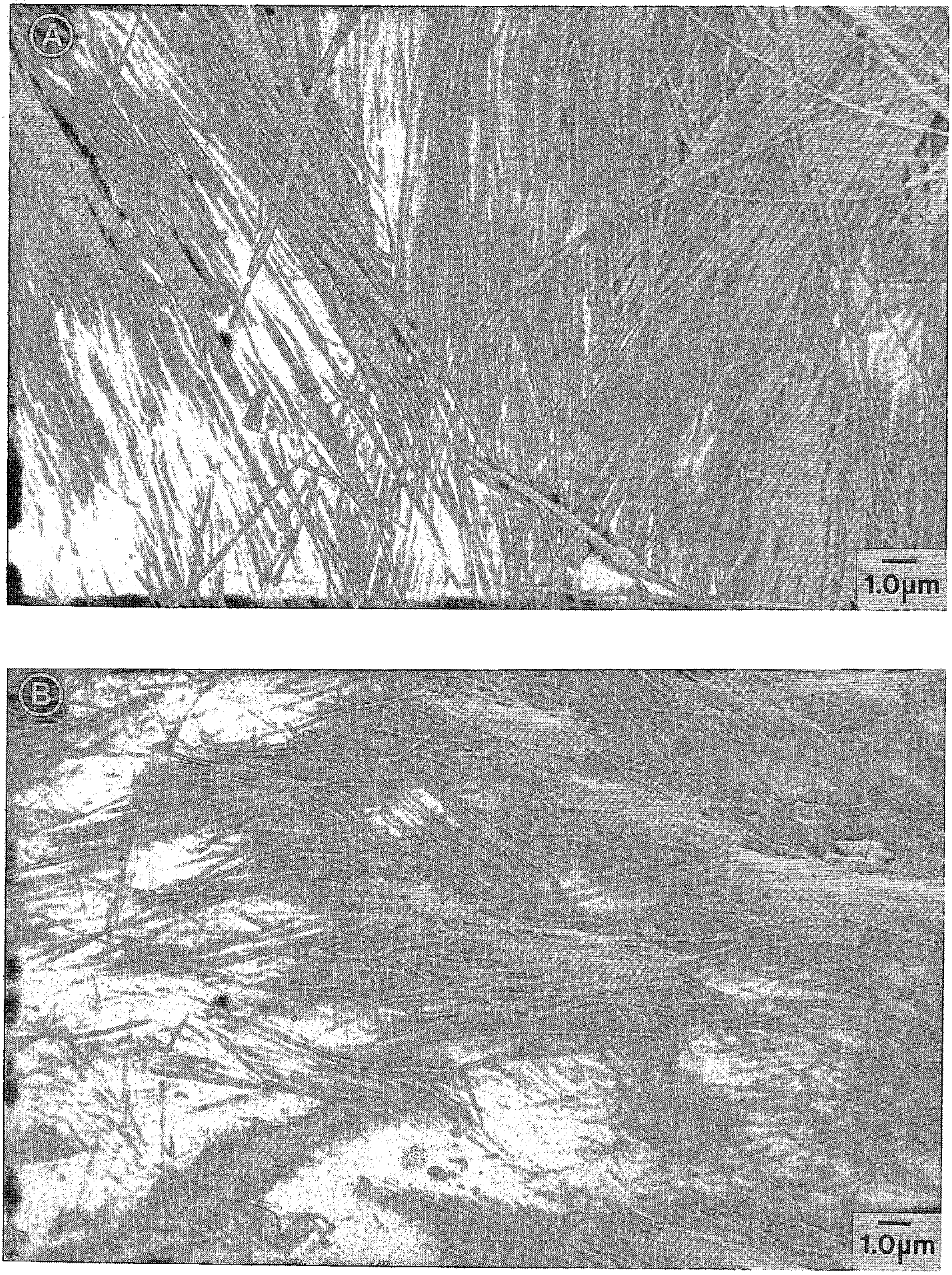

FIG. 2. Scanning electron micrograph of palygorskite showing its fibrous nature (A) and the random orientation of the fibers (B).

palygorskite-bearing fractures, but it occurs as an independent phase that can be easily separated.

Six samples of palygorskite, located at various depths listed in Table 1, were selected for detailed analysis; all samples were examined by X-ray powder-diffraction (XRD) analysis. Specimens were prepared for XRD analysis by grinding under acetone and spreading the powder into thin smear mounts; these were analyzed using Cu$K\alpha$ radiation at 30 kV and 18 mA on a Philips Norelco diffractometer. A typical X-ray diffractogram of palygorskite samples from our study area has *d* values ranging from 10.48 to 2.28 Å, and shows no shift after treatment with ethylene glycol. The observed *d* values were processed using a least-squares refinement program. The cell dimensions obtained, *a* 5.24(4), *b* 17.87(8), *c* 12.72(2) Å, compare well with the values of orthorhombic palygorskite compiled by Brindley & Brown (1980), Jones & Galan (1988), and Chisholm (1992).

The palygorskite samples are, invariably, extremely fine-grained (0.1 to 3 μm), and they show their characteristic fibrous nature (Fig. 2A), with fibers ranging in length from 3 to 50 μm. Some grains occur as equigranular aggregates, but at higher magnification these aggregates also are fibrous in character. Scanning electron micrographs of palygorskite also show random dimensional orientation, implying growth under hydrostatic and open-space environments (Fig. 2B).

Chemical and Isotopic Analysis

Methods

Six of the highest-purity (based on XRD analysis) samples of palygorskite were chosen for chemical and isotopic analysis. In view of the ubiquitous impurities present in palygorskite from various localities, as illustrated by Smith & Norem (1986), emphasis was focussed on this problem during sample selection. A smectite-group mineral (up to 5%) is the only impurity encountered in few samples of this study, and it was excluded. Analyses for the major elements (Table 1), and Rb, Sr and Th (Table 2), were carried out by X-ray-fluorescence spectrometry (XRF) at the Geological Survey of Canada, Ottawa. Total H_2O and CO_2 were determined by chemical methods. Concentrations of the rare-earth elements (*REE*) were determined by instrumental neutron-activation analysis (INAA), and U, by counting of delayed neutrons.

The activity ratios $^{234}U/^{238}U$, $^{230}Th/^{234}U$, $^{230}Th/^{238}U$ among isotopes in the uranium series were determined by isotope dilution using a fusion extraction method (Gascoyne & Larocque 1984). Samples of powdered material were spiked with ^{232}U in equilibrium with ^{228}Th as a yield tracer. The U and Th were recovered using anion-exchange techniques, extracted using TTA (thenoyltrifluoroacetone in xylene), and deposited onto stainless steel discs for α-spectrometry.

TABLE 2. CONCENTRATION OF SELECTED TRACE ELEMENTS IN PALYGORSKITE[1]

	1	2	3	4	5	6	Mean	Standard Deviation
Rb	39	44	35	30	31	28	34	6.1
Sr	464	779	508	455	519	620	557	123.4
U	11	14	10	8	9	7	9.8	2.5
Th	15	30	22	17	18	20	20.3	5.3
La	660	570	770	489	404	518	568	130.3
Ce	1120	985	1330	906	850	1005	1033	172.3
Nd	356	320	393	255	296	366	331	50.6
Sm	30.5	52.6	40.0	35.5	44.2	48.2	41.8	8.2
Eu	5.5	6.6	4.8	5.2	5.6	6.8	5.7	0.8
Gd	11.5	15.5	13.6	12.9	14.0	12.7	13.4	1.3
Tb	1.5	2.8	1.7	1.6	1.5	1.8	1.8	0.5
Ho	1.4	1.9	1.5	1.4	1.6	1.8	1.6	0.2
Tm	0.3	0.5	0.4	0.3	0.4	0.4	0.4	0.07
Yb	2.3	3.3	3.0	2.2	2.5	2.8	2.7	0.4
Lu	0.2	0.3	0.3	0.2	0.2	0.3	0.2	0.05
Y	131	157	142	136	142	155	144	10.3

Depths as in Table 1.
[1]All elements expressed in μg/g.

Oxygen was extracted from palygorskite with BrF_5, according to the procedure of Clayton & Mayeda (1963). Hydrogen isotope analyses were conducted with a modification of the procedure of Godfrey (1962). Isotopic results are reported in the conventional δ-notation, in ‰ relative to Standard Mean Ocean Water (SMOW). The precision of $\delta^{18}O$ analyses is 0.24 ‰ (2σ), and δD values are precise to 1.5 ‰ (2σ).

Compositions and Palygorskite-Forming Reaction

Chemical analyses of six samples of palygorskite from the Eye–Dashwa Lakes pluton show that it contains small but variable amounts of Ca, K and Fe^{3+}, and nearly uniform atomic proportions of Si, Mg and Al (Table 1);

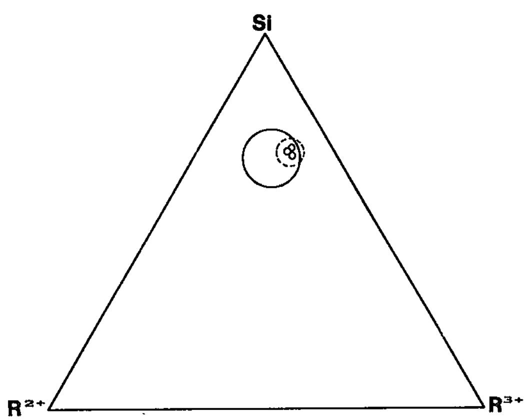

FIG. 3. Triangular plot of palygorskite compositions in terms of Si, R^{2+} (Mg) and R^{3+} (Al). Circle represents field of palygorskite delineated by Velde (1985) and Jones & Galan (1988). The smaller circle represents the field of samples analyzed in this study.

accordingly they conform to the composition of palygorskite in general (Velde 1985). These compositions, shown as a function of Si, R^{2+} (Mg) and R^{3+} (Al) ions (Fig. 3), fall within the field of palygorskite delineated by Velde (1985) and Jones & Galan (1988). The samples, however, plot preferentially along the Si–R^{3+} side of the triangle, presumably because of their paragenesis in a granitic environment. Variations in the ratio of Fe^{2+} and Fe^{3+} in the total iron, which is expressed as Fe_2O_3, may shift the data points marginally away from the Si–R^{3+} side of the triangle, but the shift still places them well inside the palygorskite field.

Although epidote is the dominant precursor that contributed to the formation of palygorskite, open-system conditions are required; the presence of significant Mg in the palygorskite (Table 1) implies that other minerals or solutes must have participated in the palygorskite-forming reaction. Chlorite, which is generally associated with epidote in minor amounts in epidote-dominated fault zones, is considered the principal source for Mg. We postulate that the palygorskite formed according to the reaction epidote + chlorite + water $\rightarrow$ palygorskite + goethite + Ca^{2+} + smectite-group mineral.

Minor and Rare-Earth Elements

Concentrations of selected trace elements found in the palygorskite samples, together with means and standard deviations, are listed in Table 2. They contain a significant amount of Sr (557 ± 123 μg/g), which probably substitutes for Ca. Large amounts of U and Th are present in palygorskite: 9.8 ± 2.5 and 20.3 ± 5.3 μg/g, respectively. These elements are probably inherited from the parental epidote. Analyses of one of the epidote samples associated with palygorskite (#2) show 30.4 μg/g U and 256 μg/g Th, which are extremely high amounts relative to those in the host granite (Table 3), where U and Th are 2.88 and 10.8 (μg/g), respectively. The Th/U ratio of palygorskite ranges from 1.36 to 2.85 and is consistently lower than the values observed in both parental epidote (Th/U = 3.75) and host rock (Th/U = 8.39). This finding indicates that U is preferentially concentrated in palygorskite relative to Th. Thorium is concentrated in goethite, which is cogenetic with palygorskite. Kamineni (1986) reported up to 38 μg/g Th in goethite associated with palygorskite.

Chondrite-normalized *REE* plots of palygorskite show steep fractionated patterns (Fig. 4). This figure also shows that the *REE* pattern of palygorskite occupies an intermediate position between chondrite-normalized patterns of epidote and host rock, and it mimics both these patterns. The host rock (ΣREE = 222) and epidote (ΣREE = 2919) patterns can be considered as two end members that contributed to the development of an intermediate pattern (ΣREE = 2000) defined by the palygorskite.

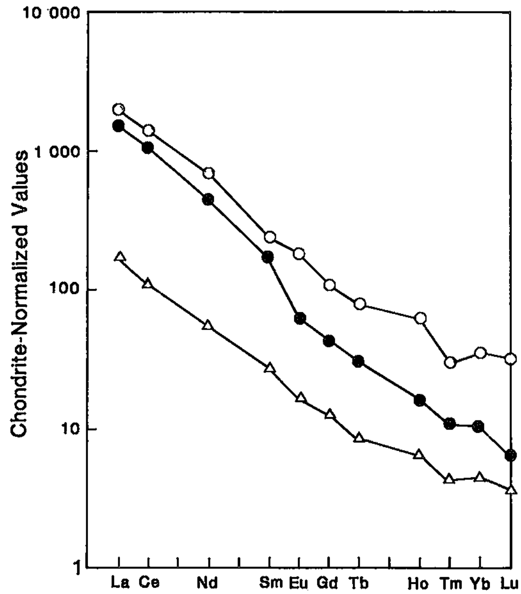

FIG. 4. Chondrite-normalized plot of *REE*s of epidote (open circles), average palygorskite (solid circles) and host rock (triangles). Concentrations of the *REE*s are normalized on the basis of Leedy values (Masuda *et al.* 1973).

TABLE 3. CONCENTRATION OF REE, U AND Th IN HOST ROCK AND EPIDOTE ASSOCIATED WITH PALYGORSKITE

REE	Host-rock (μg/g)	Epidote (μg/g)
U	2.88	30.52
Th	10.80	256
La	62.55	808
Ce	108.46	1455
Nd	41.63	520
Sm	6.58	61.50
Eu	1.50	16.11
Gd	2.90	35.50
Tb	0.49	4.50
Ho	0.58	6.20
Tm	0.15	1.17
Yb	1.15	9.80
Lu	0.15	1.28

Depth for host rock and epidote is same as palygorskite 2, i.e., 2 m.

U-Series Isotopes

The natural ^{238}U decay series is a sensitive indicator of the timing of geochemical disturbances affecting rocks within the last 1 Ma. In a closed system over a period exceeding five times the half-life of ^{234}U, the radionuclides from the ^{238}U decay chain are in secular equilibrium, with both $^{234}U/^{238}U$ and $^{230}Th/^{234}U$ activity ratios equal to unity. In contrast, if the rock is subjected to open-system interaction with fluids, the preferential mobility of ^{234}U, ^{238}U and ^{226}Ra relative to Th produces fractionation between parent and daughter isotopes, resulting in disequilibrium of activity ratios. When considering early members of the ^{238}U chain, any disequilibrium values of $^{234}U/^{238}U$ and $^{230}Th/^{234}U$ indicate migration of U-series isotopes over the last 1 Ma and 350 ka, respectively.

The analytical results for the palygorskite samples are reported as isotope activity ratios in Table 4. Figure 5 shows the quadrant plot of $^{234}U/^{238}U$ *versus* $^{230}Th/^{238}U$ (adapted from Rosholt 1983, Thiel *et al.* 1983, Latham & Schwarcz 1989).

Among the six palygorskite samples, five have $^{234}U/^{238}U$ activity ratios close to unity, indicating secular equilibrium. A clear deviation is observed only in sample 2, which has a low ratio (0.88) due to significant loss of ^{234}U. Larger variations are seen in the $^{230}Th/^{234}U$ ratios, with values close to 0.90 for samples 3 and 4, and close to 1.26 for samples 5 and 6. The $^{230}Th/^{234}U$ ratio for samples 1 and 2 are close to unity (Table 4). These

TABLE 4. CONCENTRATION OF U, Th AND ISOTOPE RATIOS*

Sample No.	U (µg/g)	Th (µg/g)	$^{234}U/^{238}U$	$^{230}Th/^{238}U$	$^{230}Th/^{234}U$
1	8.64	10.30	0.98	0.98	1.00
2	17.60	33.31	0.88	0.89	1.01
3	15.94	23.77	1.01	0.92	0.91
4	12.28	13.52	0.99	0.90	0.90
5	11.80	17.30	0.97	1.22	1.26
6	12.25	18.18	0.95	1.18	1.24

*All isotopic ratios are at 1σ uncertainty ± 0.02
Depths as in Table 1.

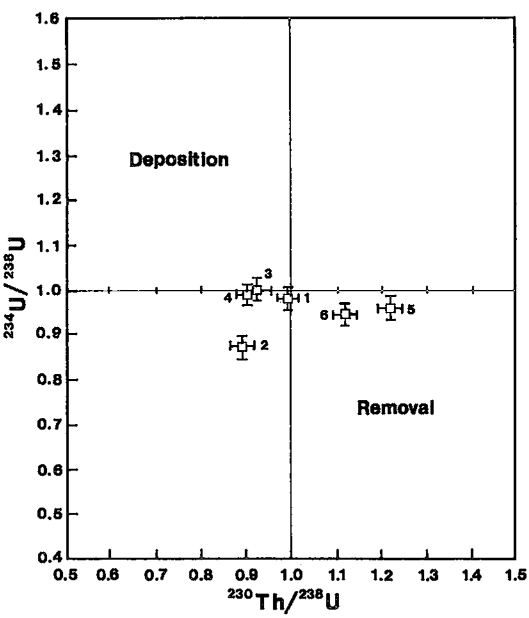

FIG. 5. Plot of $^{234}U/^{238}U$ *versus* $^{230}Th/^{238}U$ for palygorskite.

variations in $^{230}Th/^{234}U$ isotope ratios indicate that some geochemical disturbances affecting palygorskite have occurred in recent geological time, over the last 350 ka. Samples 5 and 6 have high $^{230}Th/^{238}U$ ratios, but equilibrium values for $^{234}U/^{238}U$ (Fig. 5), which indicate a general removal of U with no preferential loss of ^{234}U compared to ^{238}U. Interestingly, these samples are from the shallowest depths below ground surface, where shallow groundwaters appear to move at a rapid rate. In contrast, low $^{230}Th/^{238}U$ and $^{234}U/^{238}U$ ratios of ~ 1 in samples 3 and 4 indicate a general deposition of U. These two samples are from about 7 m below samples 5 and 6. The locations of samples 3, 4, 5 and 6 and the U-series isotope characteristics suggest that the U removed from surface or near surface (in samples 5 and 6) is concentrated in deeper regions of the fracture zone (in samples 3 and 4).

Samples 1 and 2, which are located at the deepest position (~ 25 m) in the fracture zones investigated, behave differently. No isotopic disequilibrium is present in sample 1, suggesting lack of recent migration of U in this fracture. In contrast, sample 2 reflects some loss of ^{234}U to groundwater within the last 1 Ma, as shown by $^{234}U/^{238}U$ ratio (0.88). However, as the $^{230}Th/^{234}U$ ratio is close to unity, the process involved in ^{234}U loss without total leaching of U must be caused by the α-recoil process from surface sites on the mineral (Fleischer 1988, Gascoyne 1982).

An approximate rate of leaching of ^{238}U and ^{234}U can be calculated for samples 5 and 6, using equations of Latham & Schwarcz (1987) for weathering processes. Samples 5 and 6 collected from near-surface fracture zones have been exposed to circulation of meteoric water. When groundwater moves through the fracture periodically, U leaching resumes. Because water flow must occur within a period of time shorter than the half life of ^{230}Th (7.5×10^4 a), the removal of U can be considered as a continuous process. A secular equilibrium is reached after five half-lives of ^{234}U, which is ~ 1 Ma. Then, the rate of leaching can be approximated using the equations of Latham & Schwarcz (1987):

$$C_8 = \lambda_0 \left[1 - \frac{1}{^{230}Th/^{234}U}\right]$$

$$C_4 = \lambda_4 \left[\left(\frac{1}{^{234}U/^{238}U} - 1\right) + \lambda_0 \left(1 - \frac{1}{^{230}Th/^{234}U}\right)\right]$$

where C_8 and C_4 are the leach rates of ^{238}U and ^{234}U, respectively, and λ_o and λ_4 are the decay constants of ^{230}Th and ^{234}U. These equations were formulated assuming no leaching of ^{230}Th, which is an element of low mobility (Langmuir & Herman 1980).

Using the activity ratios in Table 4, and assuming equilibrium, the rates of leaching for ^{238}U and ^{234}U for samples 5 and 6 are: $C_8 = 1.84\ 10^{-6}\ a^{-1}$, and $C_4 = 1.96 \times 10^{-6}\ a^{-1}$. The resulting activity ratios are presented in Figure 6.

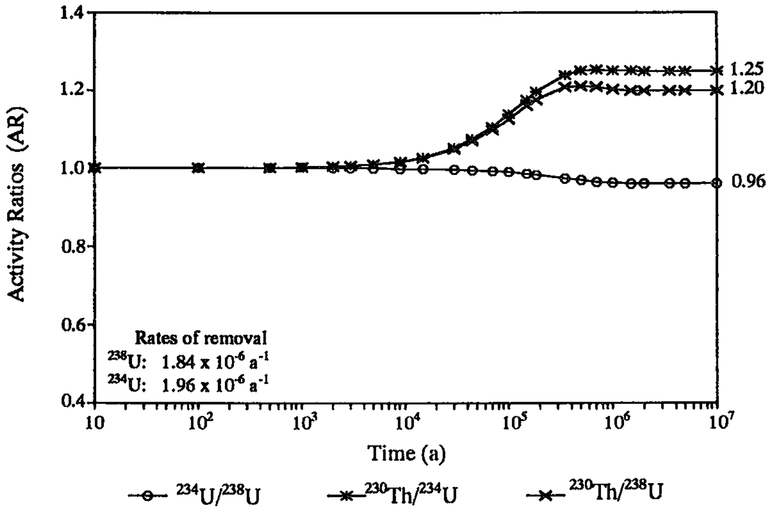

FIG. 6. Plot of activity ratios $^{234}U/^{238}U$ and $^{230}Th/^{234}U$ *versus* time (a).

During this time, the palygorskite would have been losing U at an exponential rate controlled by C_8 ($U_8 = {}^{\circ}U_8 e^{-C_8 t}$). Accordingly, palygorskite should have lost about 50% of its U in 400,000 years, but its total concentration of uranium (≈8 μg/g), which is only slightly lower than in other samples, suggest otherwise. Values of $^{230}Th/^{234}U$ between 1 and 1.2 are typical of weathered samples below the surface (Gascoyne 1982). Samples 5 and 6 indeed fall in this category. According to Latham & Schwarcz (1987), samples from the surface have $^{230}Th/^{234}U$ ratios between 1.2 and 1.8; because of the high hydraulic permeability in these shallow regions, such equilibrium values (*i.e.*, 1.2 and 1.8) can be attained within 10,000 years. Such values generally are interpreted to be due to large removal of labile U from the rock *i.e.*, U on the grain surfaces. Replacement of epidote by palygorskite is likely to have occurred less than or about 1 Ma ago (Kerrich & Kamineni 1988), suggesting that a ratio of 1.25 for $^{230}Th/^{238}U$ in the latter was attained within a time shorter than 1 Ma, resulting in overestimation of C_8 in our calculation. As discussed by Latham & Schwarcz (1987), this overestimation can result from the presence of easily removable U. This implies that U is located on palygorskite surfaces rather than in its structure.

STABLE ISOTOPE RELATIONSHIPS

Collectively, the palygorskite samples are characterized by δD and $\delta^{18}O$ values that span –75 to –128 and 18.4 to 23.4‰, respectively (Table 5). The majority of samples have relatively uniform $\delta^{18}O$ values, between 21.9 to 23.4‰, with a relatively large range of δD values that vary more or less systematically from –128‰ at the surface to –75‰ at depth, and define a vertical trend in δD *versus* $\delta^{18}O$ coordinates (Fig. 7). These data are difficult to interpret in the absence of experimentally determined mineral–water fractionations for palygorskite, and estimates of formation temperatures.

Palygorskite is a member of one of five clay mineral groups, the remainder being the kaolinite, illite, smectite and vermiculite groups (Deer *et al.* 1966). At ≤50°C, differences in the oxygen isotope mineral–water fractionations for smectite, kaolinite and illite are less than 5‰, at any specified temperature. Similarly, hydrogen isotope mineral–water fractionations of kaolinite and smectite are within 10‰ at ≤50°C (Figs. 18 and 19 in Kyser 1987). Accordingly, we assume that the palygorskite–water fractionations approximate those of smectite–water to within a few ‰. Given the restriction of palygorskite to low-temperature, near-surface environments, limiting temperatures of formation between 0° to 25°C are assumed.

One of the palygorskite samples (#2) plots near a low-temperature equilibrium clay–water line, and this sample also plots close to previously analyzed mixtures of kaolinite, halloysite and palygorskite from fracture fillings in the Eye–Dashwa Lakes pluton (Kerrich &

TABLE 5. OXYGEN AND HYDROGEN ISOTOPE COMPOSITIONS OF PALYGORSKITE

Sample No.	$\delta^{18}O$ ‰	δD ‰
1	23.1	-75
2	18.4	-85
3	21.9	-95
4	23.4	-125
5	23.4	-120
6	22.7	-128

Depths as in Table 1.

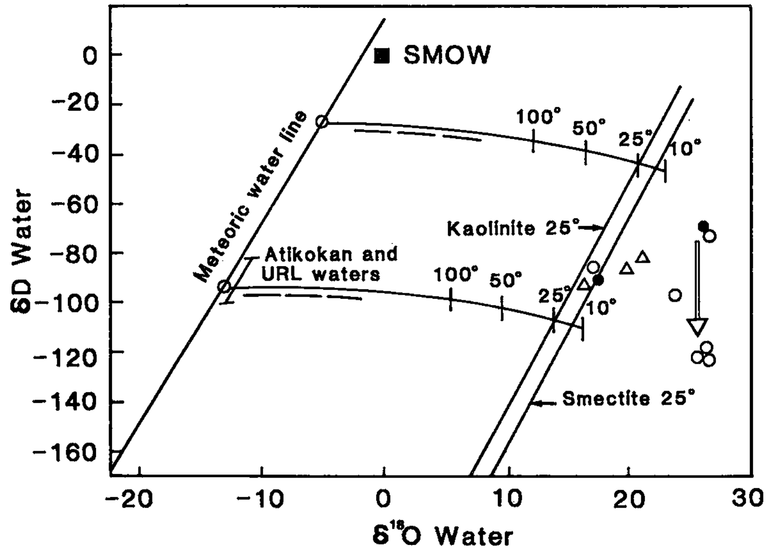

FIG. 7. Stable isotope composition of meteoric water and standard mean ocean water (SMOW). Also shown are the range of Atikokan and Underground Research Laboratory (URL) waters (see Kerrich & Kamineni 1988). Kaolinite and smectite lines are from Kyser (1987). Solid circles: results of previous analyses of kaolinite, halloysite and palygorskite (after Kerrich & Kamineni 1988); triangles: illite from URL; open circles: palygorskite from present study. Arrow represents trend of deuterium depletion.

Kamineni 1988). Collectively, those samples formed in or close to equilibrium with modern groundwaters at Atikokan, where δD H_2O is between –80 and –100‰, and $\delta^{18}O$ H_2O, between –10 and –12‰ (Fig. 7).

The group of five samples that form a vertical trend on Figure 8, to the right of the low-temperature clay line, requires a two-stage history. An alternative explanation is that the isotopically anomalous samples of palygorskite initially formed in the presence of fluids more ^{18}O- and D-enriched than present surface-waters. Subsequently, they experienced variable degrees of H-isotope exchange with depleted surface-waters in the absence of O-isotope exchange. This interpretation is supported by the trend of decreasing δD values with depth, such that near-surface samples underwent the largest shifts in δD.

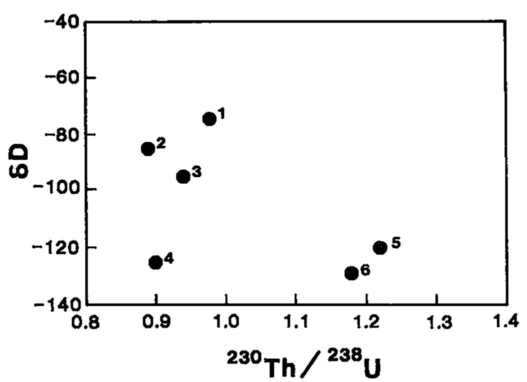

FIG. 8. Plot of δD *versus* $^{230}Th/^{238}U$ for palygorskite. Excluding sample 4, a negative correlation is apparent.

Wilson & Kyser (1987) and Kotzer & Kyser (1991) have previously reported anomalously low-δD serpentines and clay minerals in rocks from the Canadian Shield. These were interpreted to have formed under one set of conditions, and subsequently exchanged H (but not O) with D-depleted meteoric waters at low temperatures in the near-surface environment, thereby generating a vertical trend in δD *versus* $\delta^{18}O$ coordinates (for a review, see Kyser & Kerrich 1990).

Samples 5 and 6, which are characterized by removal of U, also show relative depletion in D. Plots of δD *versus* $^{230}Th/^{238}U$ and δD *versus* $^{230}Th/^{234}U$ substantiate this correlation. For example, with the exception of sample 4, a decrease in δD is associated with greater values of $^{230}Th/^{238}U$ and $^{230}Th/^{234}U$, which implies removal of both ^{238}U and ^{234}U (Figs. 8, 9). At present, we are uncertain about the process(es) that conserved isotopes of U in sample 4 despite its low δD values, but the processes of U removal and proton exchange are different.

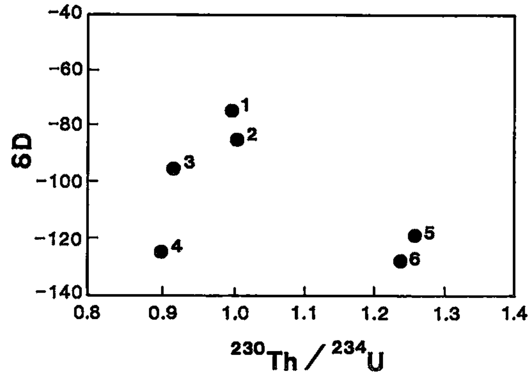

FIG. 9. Plot of δD *versus* $^{230}Th/^{234}U$ for palygorskite. Excluding sample 4, a negative correlation is apparent.

SUMMARY AND CONCLUSIONS

(1) Palygorskite in fracture zones of the Eye–Dashwa Lakes granitic pluton formed by alteration of pre-existing epidote. Chemically, the analyzed samples of palygorskite define a tight range and plot within the compositional field defined for this species; they are enriched in the light rare-earth elements. The chemistry of the palygorskite suggests that, in addition to epidote, a Mg-bearing phase such as chlorite or Mg-bearing solute must have participated in its formation.

(2) The $^{234}U/^{238}U$ ratios of palygorskite samples cluster around unity, implying secular equilibrium, whereas samples located at higher elevation contain greater $^{230}Th/^{234}U$ ratios, indicating geochemical disturbance in recent times (within the last 350 ka). The latter is reflected in uranium removal in these samples, and also correlates with greater hydraulic permeability in the field.

(3) Stable isotope characteristics of the palygorskite are generally compatible with those of the clay-mineral group and indicate formation in equilibrium with modern groundwaters. The samples occurring very near the surface have experienced preferential exchange of H isotopes, and this produced a trend of decreasing δD with depth.

ACKNOWLEDGEMENTS

The authors thank C.C. Davison and D. Oscarson for incisive critique of an earlier draft, and for suggestions that improved the manuscript. We thank D. Pezderic for assistance with the stable isotope analyses, R.N. Delabio with X-ray diffractometry, P. Bélanger for chemical analysis, and D. Doern for SEM. D.C. Kamineni and L.Y. Griffault were jointly funded by AECL Research and Ontario Hydro under the auspices of the CANDU Owners Group. We acknowledge an NSERC operating grant to R. Kerrich, an NSERC Infrastructure grant to R. Kerrich and T.K. Kyser, and the George McLeod endowment to the Department of Geological Sciences, University of Saskatchewan. Reviews by Jim Chisholm, Robert F. Martin and an anonymous reviewer benefitted this paper.

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* Unpublished report available from SDDO, AECL Research, Chalk River, Ontario K0J 1J0.

Received August 7, 1991, revised manuscript accepted March 18, 1992.