1   **Appendix**

2

3   **1 - Detailed equations for the determination of ^{40}K content in mineral**

4   Considering M as the molecular weight (in g/mol)

5

6   - %K content expressed in g / g of mineral i

7

8    $$\% K_{(g/g_i)} = \frac{(\% K_2O)_i \times M_K \times 2}{M_{K_2O}} \quad \text{(A)}$$

9

10   - %K content expressed in mole / mole of mineral i

11

12   $$\% K_{(moles/moles_i)} = \frac{\% K_{(g/g)} \times M_i}{M_K} = \frac{(\% K_2O)_i \times M_i \times 2}{M_{K2O}} \quad \text{(B)}$$

13

14   - %^{40}K content determination using ^{40}K/K ratio = 0.01167 x 10^{-2} (Garner at al., 1975) – Unit

15   in mole / mole of mineral i

16   $$\% ^{40}K_{(moles/moles_i)} = \frac{(\% K_2O)_i \times M_i \times 2}{M_{K2O}} \times (0.01167 \times 10^{-2}) \quad \text{(C)}$$

17

18   - %^{40}K content expressed in mole / mole of the mixture, with X = % sericite in the melange

19

20   $$\% ^{40}K_{(moles/moles_{mel})} = X ^{40}K_{(moles/moles_i)} \quad \text{(D)}$$

21

22   - <u>Numerical application for the ^{40}K$_{Ser}$</u>

23

24   M$_{Ser}$ = Molecular Weight of empiric sericite (KAl$_3$Si$_3$O$_{10}$(OH)$_2$) = 398.31 g/mol
25   M$_{K2O}$ = Molecular Weight of K$_2$O= 94.2 g/mol
26   M$_k$ = Molecular Weight of K = 39.1 g/mol
27   ^{40}K/K = 0.01167 x 10^{-2}
28   %K$_2$O = 11.82 %; %K = 9.82%

29

30   Equation A : *%K (g/g$_{ser}$) = 0.098 %*
31   Equation B : *%K (moles/moles$_{ser}$) = 0.999 %*
32   Equation C : *%^{40}K (moles/moles$_{ser}$) = 1.166 x 10^{-4} %*

33

34   Note that "sericite" term is used as a general description for fine-grained phyllosilicate

35   replacement phases. Sericite does not have a fixed composition and can been reported as

36   paragonite, illite, or hydromuscovite. The majority of sericite is K-bearing, but clearly not

37 <u>fixed exactly at 11.82% K_2O as used in the present model (pure muscovite). It is a</u>
38 <u>adjustable parameter in the model which can be given by in situ microprobe analysis.</u>

39

40
41
42
43
44 - <u>Numerical application for the ${}^{40}K_{Pl}$</u>
45

46 Unlike the sericite, which has a fixed chemical composition, plagioclases have various Ca,

47 Na and thus K contents. Thus, we have to determine the %K_2O in plagioclase regarding

48 their various Na and Ca contents.

49 Structural formula of plagioclases can be expressed as:
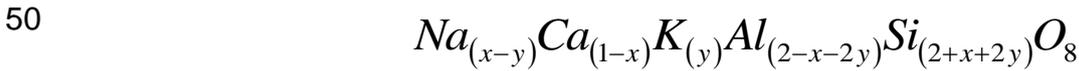
50
$$Na_{(x-y)}Ca_{(1-x)}K_{(y)}Al_{(2-x-2y)}Si_{(2+x+2y)}O_8$$
51

52 For each x and y value, *i.e* for each plagioclase composition ranging from pure end-

53 member of albite (An$_0$) to anorthite (An$_{100}$), we can calculate the proportion of K related to

54 those of Ca and Na. The K content in common plagioclase rarely exceeds 5% of the K-rich

55 end-member (see Figure A). We can realistically consider that the stoichiometric indice y is

56 ranging from 0 to 0.05.
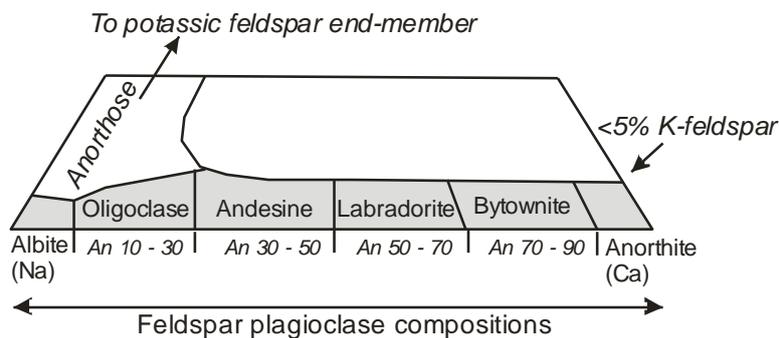
57

58 Figure A: Classification of plagioclases

59

60 Thus, we can model various composition of plagioclases, based on their structural formula

61 which gives us the related (1) molecular weight, (2) the %K_2O and (2) the Ca/K of the

62 plagioclase (see table A, figures B & C, and see Part. 3 of appendix for detailed

63 explanations). For example, y values ranging from 0.001 to 0.05 implies that related K_2O

64 contents for classical plagioclases range from 0.0017% to 0.87% using an An_{50} value for

65 this plagioclase (Figure B). For an An_{05}, calibrated values are also shown in Figure C.

66 By knowing the molecular weight and related %wt K_2O for all theoretical plagioclases, we

67 can apply the previous equations A, B, and C (Table A).
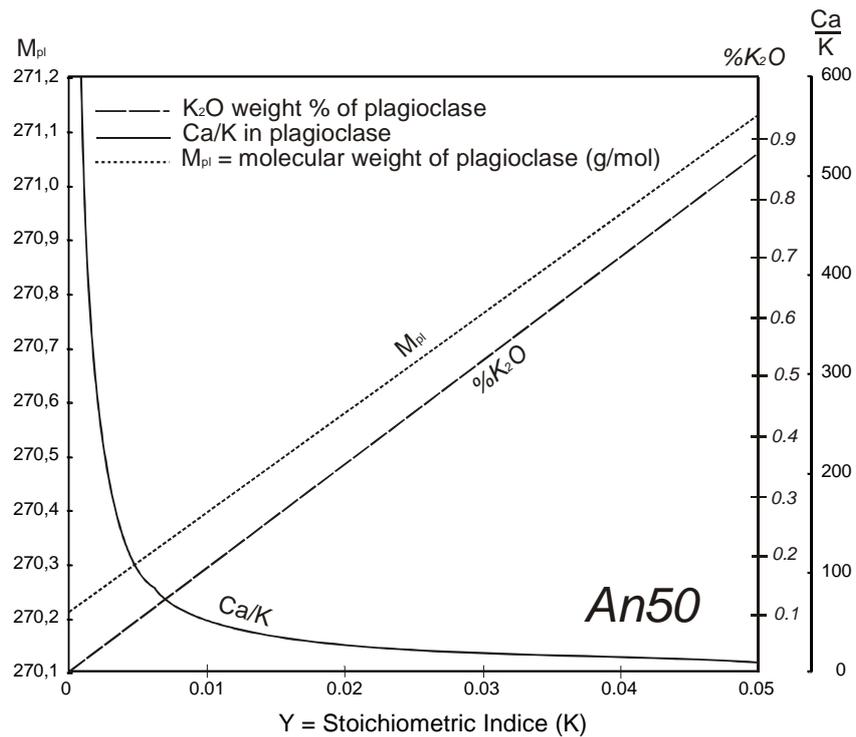
Figure B: Related molecular weight, % wt K_2O and Ca/K values in the case of An_{50}
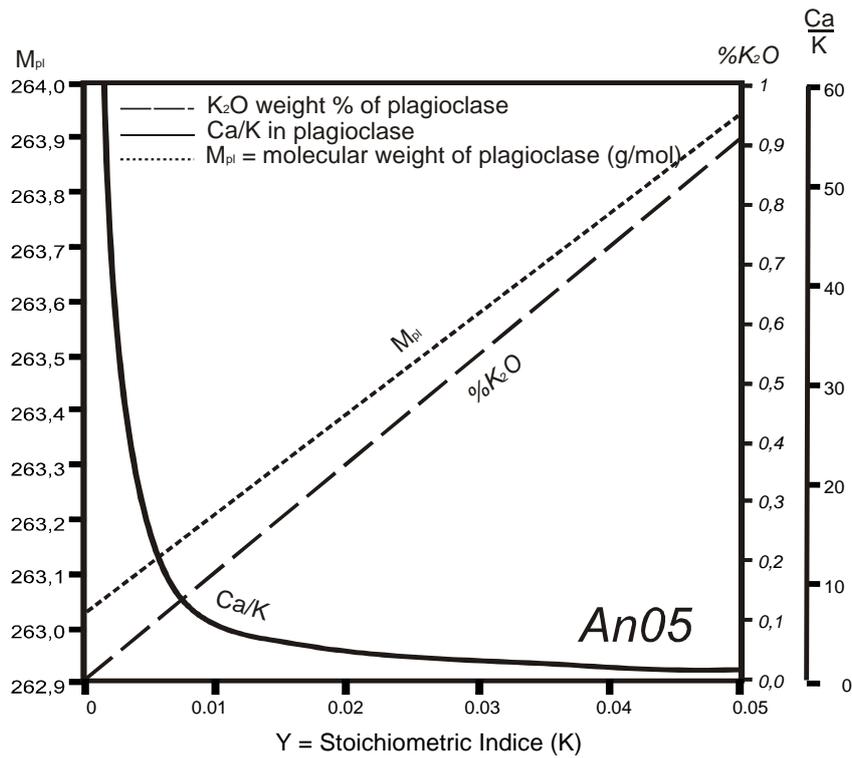
Figure C: Related molecular weight, % wt K_2O and Ca/K values in the case of An_{05}

	Example #1	Example #2	Example #3
PLAGIOCLASE	K-rich An_{50}	K-poor An_{50}	Classical An_{50}
Structural formula	$K_{0.05}Na_{0.45}Ca_{0.5}Si_{2.6}Al_{1.4}$	$K_{0.001}Na_{0.499}Ca_{0.5}Si_{2.502}Al_{1.498}$	$K_{0.01}Na_{0.490}Ca_{0.5}Si_{2.52}Al_{1.48}$
y (stoichiometric indice)	0.05	0.001	0.01
%wt K_2O	0.869	0.017	0.174
Molecular weight in g/mol	271.13	270.23	270.40
Related mass ratio Ca/K	10	500	50
Equation A	0.72140	0.01411	0.14444
Equation B	5.0024	0.0975	0.9989
Equation C	$5.84\,e^{-4}$	$1.14\,e^{-5}$	$1.17\,e^{-4}$

Table A: Some examples of calculated values for plagioclases An_{50}
Equations A, B & C are applied using: M_{K2O} = molecular weight of K_2O= 94.2 g/mol; M_k = molecular weight of K = 39.1 g/mol; $^{40}K/K$ = 0.01167 x 10^{-2} (Garner et al., 1975)

2 - Detailed equations for the determination of $\left(\dfrac{^{40}K_{Ser}}{^{40}K_{Tot}}\right)$ **and** $\left(\dfrac{^{40}K_{Pl}}{^{40}K_{Tot}}\right)$ **in the mixture**

80 Using Equation (D) and Equation (1) $^{40}K_{tot} = (1-X)^{40}K_{Pl} + X^{40}K_{Ser}$, we determine the two

81 ratios for the mixture as following :

$$\left(\frac{^{40}K_{Ser}}{^{40}K_{Tot}}\right) = \frac{X \times \left(\frac{\%K_2O_{Ser} \times M_{Ser} \times 2 \times 0.0001167}{M_{K_2O}}\right)}{(1-X) \times \left(\frac{\%K_2O_{Pl} \times M_{Pl} \times 2 \times 0.0001167}{M_{K_2O}}\right) + X \times \left(\frac{\%K_2O_{Ser} \times M_{Ser} \times 2 \times 0.0001167}{M_{K_2O}}\right)} =$$

$$\frac{X \times (\%K_2O_{Ser} \times M_{Ser})}{(1-X) \times (\%K_2O_{Pl} \times M_{Pl}) + X \times (\%K_2O_{Ser} \times M_{Ser})} (E)$$

83

84 and also :

$$\left(\frac{^{40}K_{Pl}}{^{40}K_{Tot}}\right) = \frac{(1-X) \times (\%K_2O_{Pl} \times M_{Pl})}{(1-X) \times (\%K_2O_{Pl} \times M_{Pl}) + X \times (\%K_2O_{Ser} \times M_{Ser})} (F)$$

86

87

88 **3 – Relationship between %wt K$_2$O, %wt CaO and Ca/K in plagioclase**

89 It is obvious that these three chemical parameters are not independent in plagioclase, such

90 as shown in Figures B and C. In equation (E) and (F), the Ca/K ratio is missing, although it

91 is very important in Ar-Ar dating, because it is related to the $^{37}Ar_{Ca}/^{39}Ar_K$ ratio measured

92 during degassing process of analyzed minerals.

93 If we apply equations (A) and (B) for Ca in plagioclase:

94

95 $$\%Ca_{(g/g_{Pl})} = \frac{(\%CaO)_{Pl} \times M_{Ca}}{M_{CaO}} \text{ and } \%Ca_{(mol/mol_{Pl})} = \frac{(\%CaO)_{Pl} \times M_{Pl}}{M_{CaO}}$$

96
97 We can determine the $(Ca/K)_1$ mass ratio or $(Ca/K)_2$ molar ratio as following :

98 $$\left(\frac{Ca}{K}\right)_1 = \frac{(\%CaO)_{Pl} \times M_{Ca}}{M_{CaO}} \times \frac{M_{K_2O}}{2 \times (\%K_2O)_{Pl} \times M_K} \approx 0.8606 \left(\frac{\%CaO}{\%K_2O}\right)_{Pl}$$

99
$$\left(\frac{Ca}{K}\right)_2 = \frac{(\% CaO)_{Pl} \times M_{Pl}}{M_{CaO}} \times \frac{M_{K_2O}}{2 \times (\% K_2O)_{Pl} \times M_{Pl}} = \frac{(\% CaO)_{Pl} \times M_{K_2O}}{2 \times M_{CaO}(\% K_2O)_{Pl}} \approx 0.8387 \left(\frac{\% CaO}{\% K_2O}\right)_{Pl}$$

100

101 Consequently, we can write taking into account the molar ratio:

102
$$(\% K_2O)_{Pl} = \frac{M_{K_2O}}{2M_{CaO}} \times (\% CaO)_{Pl} \times \left(\frac{K}{Ca}\right)_{Pl} \quad (G)$$

103 If we use equation (G) in equations (E) and (F), we obtain the final equations used in our

104 model:

105
$$\left(\frac{^{40}K_{Ser}}{^{40}K_{Tot}}\right) = \frac{X(\% K_2O_{Ser} \times M_{Ser})}{(1-X)\left(\frac{M_{K_2O}}{2M_{CaO}} \times (\% CaO)_{Pl} \times \left(\frac{K}{Ca}\right)_{Pl} \times M_{Pl}\right) + X(\% K_2O_{Ser} \times M_{Ser})} \quad (H)$$

106
$$\left(\frac{^{40}K_{Pl}}{^{40}K_{Tot}}\right) = \frac{(1-X)\left(\frac{M_{K_2O}}{2M_{CaO}} \times (\% CaO)_{Pl} \times \left(\frac{K}{Ca}\right)_{Pl} \times M_{Pl}\right)}{(1-X)\left(\frac{M_{K_2O}}{2M_{CaO}} \times (\% CaO)_{Pl} \times \left(\frac{K}{Ca}\right)_{Pl} \times M_{Pl}\right) + X(\% K_2O_{Ser} \times M_{Ser})} \quad (I)$$

107 The %wt CaO for plagioclase is related to stoichiometric indice of Ca in the structural

108 formula. For our model mixing, we fixed first on An_{70}, of An_{10}, or $An_{30...}$ for a given K content

109 (y stoichiometric indice) and we calculated the related %wt CaO, Ca/K ratio and thus the

110 induced molecular weight of the considered plagioclase (example in table A). We input

111 these values in equations (H) and (I).

112

113 **4- Determination of the sericitization value (X) in $^{40}Ar/^{39}Ar$ spectra**

114 With the $^{37}Ar_{Ca}/^{39}Ar_K$ data from a real experiment, we approximate the Ca/K ratio of the

115 mélange $(Ca/K)_{mel}$ respect to Ca/K and related $\%^{39}Ar$ of each temperature steps :

116
$$\left(\frac{Ca}{K}\right)_{mel} = \sum_1^i \left(\%^{39}Ar_i \times \left(\frac{Ca}{K}\right)_i\right) = s \quad (J)$$

117   with i = number of steps

118   and Ca/K=1.83 x $^{37}Ar_{Ca}/^{39}Ar_K$ (after McMaster reactor facilities)

119   We can also define the theoretical value $(Ca/K)_{mel}$ considering the $(Ca/K)_{Pl}$ of the unaltered

120   plagioclase:

121
$$\left(\frac{Ca}{K}\right)_{mel} = \frac{Ca_{Pl}}{K_{Pl} + K_{Ser}} = \frac{\left(\dfrac{Ca}{K}\right)_{Pl}}{\left(1 + \dfrac{K_{Ser}}{K_{Pl}}\right)} \qquad (K)$$

122   With Equations (2) and (3), we can replace K_{Ser}/K_{Pl} with :

123
$$\left(\frac{Ca}{K}\right)_{mel} = \frac{\left(\dfrac{Ca}{K}\right)_{Pl}}{\left(1 + \dfrac{XB}{(1-X)AC}\right)} = s \qquad (L)$$

124
$$\text{With } C = \left(\% CaO\right)_{Pl} \times \left(\frac{K}{Ca}\right)_{Pl} \times M_{Pl}$$

125   And with known value = Ca/K of the fresh plagioclase

126   Finally, we obtain:

127
$$X = \frac{1}{\left(\dfrac{B}{\gamma AC}\right) + 1} \quad \text{with} \quad \gamma = \frac{\left(\dfrac{Ca}{K}\right)_{Pl}}{\displaystyle\sum_{1}^{i}\left(\%\,^{39}Ar_i \times \left(\dfrac{Ca}{K}\right)_i\right)} - 1 = \left(\frac{\left(\dfrac{Ca}{K}\right)_{Pl}}{s} - 1\right) \qquad (M)$$

128
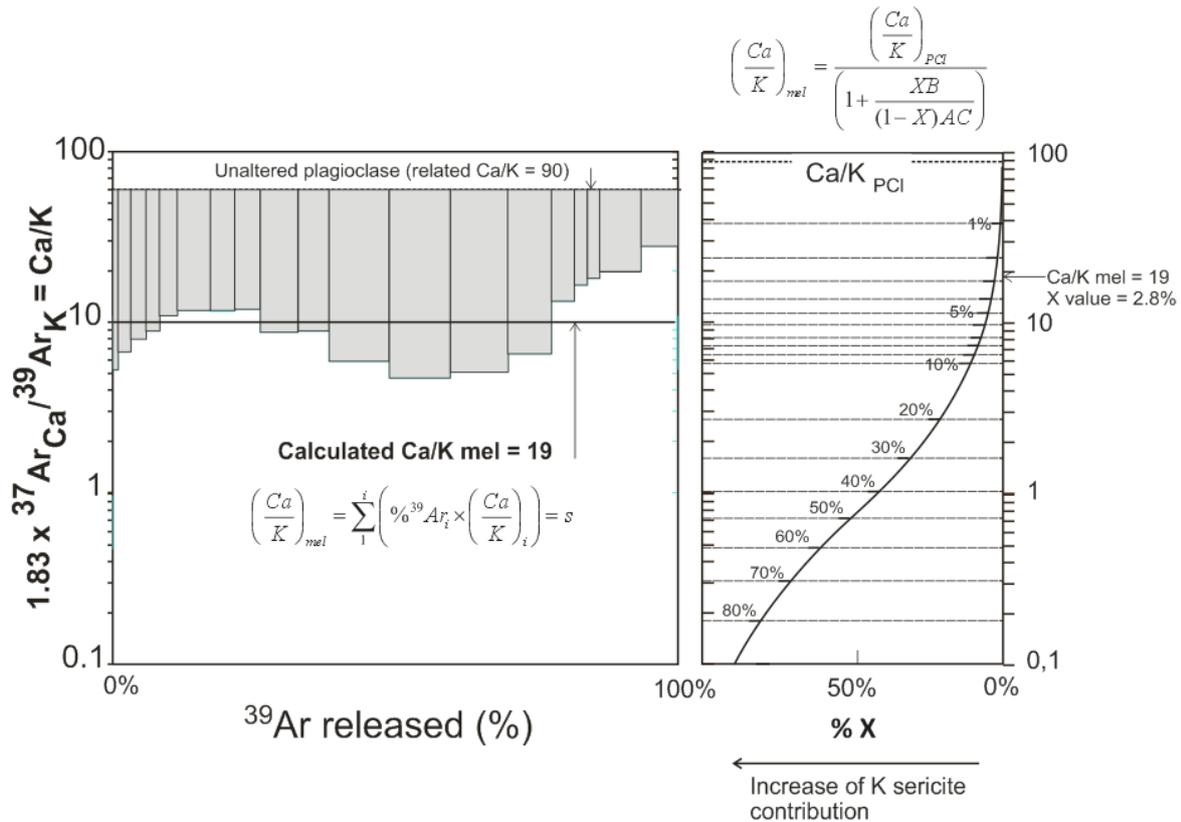
129   We use these equations for $^{40}Ar/^{39}Ar$ data reported in figures 6 and 7.

130   For the CAMP plagioclase (figure 6), we find a degree of sericitization of ~3% (see figure

131   D). For Karoo sample, we find a slight sericitization of 0.16% (figure 7).

132

Figure D: Ca/K spectrum (left) of plagioclases from the Central Atlantic Magmatic Province; and theoretical $(Ca/K)_{mel}$ using equation K (right). The (Ca/K) of the melange is determined using equation (J) and corresponds to 2.8% of sericitization.

5- Estimate of the age t' of the alteration in Ar-Ar spectra

Using equation (1) in the text, and considering previous X value in equations (2) and (3), we can write for t':

$$t' = \frac{1}{\lambda} \ln\left[1 + \left(\frac{^{40}K_{tot}}{^{40}K_{Ser}}\right)(e^{\lambda t_{mel}} - 1) - \left(\frac{^{40}K_{Pl}}{^{40}K_{Ser}}\right)(e^{\lambda t} - 1)\right] \quad (N)$$

with t = age of the unaltered plagioclase and t_{mel} = age of the mélange and thus the total gas age during the entire degassing process (for i temperature steps):

145
$$t_{mel} = \sum_{1}^{i} \left(\%\,{}^{39}Ar_i \times t_i \right)$$
(O)

146 For CAMP and Karoo plagioclases, we find an age of sericitization of 176 My and 172 My,

147 respectively.

148