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Anomalous fading parameters and activation energies of feldspars

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Abstract

Anomalous fading parameters and activation energies are reported for a variety of feldspars and K-feldspars separated from sediments. While some interesting patterns emerge, prediction of the fading parameter from a measurement of the activation energy would appear to be unwise. There was a tendency for the activation energy to increase from 0.04 to 0.2 eV as the K content increases from 0 to 15 %.

Introduction

Anomalous fading in feldspars is characterized by a decrease in the luminescence intensity measured during optical or thermal excitation as the delay time between irradiation and measurement increases. This decrease is not expected on the basis of measured thermal kinetic parameters and is, to a good approximation, linearly dependent on the logarithm of elapsed time since irradiation. Anomalous fading is now generally recognised as being due to the tunnelling of electrons from the ground state of the principal trap to nearby defects.

Quantitatively, anomalous fading is described by the fading parameter, g, which is the fractional decrease per decade, a decade here being a factor ten of time. Formally,

$$I = I_c(1 - g\log(t/t_c)) \qquad (1)$$

where I is the intensity at time t and I_c is the intensity at an arbitrary time t_c. Thus g depends on the choice of t_c, though weakly.

The activation energy referred to here is a completely unrelated concept. In 1988, Hütt et al. made the observation that the luminescence intensity caused by 1.4 eV excitation increases with temperature. This increase is well described by the Arrhenius equation,

$$I = C\exp(-E/kT), \qquad (2)$$

from which an activation energy, E, may be obtained for a sample. Despite several attempts to explain this effect, the underlying cause is as yet unknown.

There were two motivations for the present measurements. The first was that our measurements of anomalous fading make use of a control sample, referred to as a témoin, which should not fade, to correct for any changes in the instrument sensitivity and decay during luminescence measurements. The intensities of both the témoin and the sample increase with temperature. If the laboratory temperature changes from one measurement to another and the témoin and sample have different activation energies, then an error in the calculated fading parameter will occur unless this is corrected for. The effect can be quite significant. Since we have little control over our laboratory temperature we measured activation energies so that we can make the appropriate corrections. A better solution would be to control the laboratory temperature to 1 ºC or less.

The second motivation was the possibility that the activation energy might be related in some unknown way to the tunnelling, and that there might be a relation between g and E. This possibility has been suggested by Poolton et al. (2003) who described some evidence for it. If such a relation existed then the lengthy measurements required to obtain g could be replaced by a simple measurement of E, an attractive proposition.

Anomalous fading: experimental procedure

Measurements of the fading parameter g were as described in Huntley and Lamothe (2001), method ‘b’. Aliquots were prepared by attaching thin slices of the minerals, or approximately 12 mg of K-feldspar grains separated from a sediment, to aluminium planchets using a Crystalbond[1]-acetone mixture and drying the planchet in the oven for one hour at 50 ºC.

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[1] Crystalbond 509: Aremco Products Inc., P.O. Box 517, 707-B Executive Blvd., Valley Cottage, N.Y. 10989, U.S.A.

Five aliquots of each sample were bleached if necessary, given a gamma dose of ~175 Gy using a Nordion ^{60}Co Gammacell[2], heated at 120 ºC for 16 hours, and measured using short shines at ca 2, 4, 8, 16, etc. days to about a year after irradiation. Excitation was 1.4 eV (IR) from LEDs and emission was measured using a Thorn-EMI 9635QB photomultiplier with Schott BG39 and Kopp 5-57 filters. This is designed to measure the violet emission band that is characteristic of K-feldspars. The témoin were K-feldspars separated from Tertiary sandstone from China Beach, Vancouver Island, British Columbia, sample CBSS.

Activation energy: experimental procedure

A detailed description of the equipment used for these measurements is given by Short (1993). Measurements were made using a conventional (Oxford style) thermoluminescence oven, over which was positioned an array of 1.4 eV (infrared) LEDs used to excite the sample. To avoid significant depletion of trapped charge, the LED array was pulsed. Emission from the sample passed through the centre of the diode array and was measured using a Thorn-EMI 9635QB photomultiplier tube with Schott BG-39 and Kopp 5-60 filters, similar to that in the first experiment.

For measurement, an aliquot previously used for the anomalous fading measurement was placed on the heating strip, using thermal compound to obtain a good thermal contact. Control for the experimental setup was automated by a PC running a program that controlled the power to the heating strip, pulsed the LED array and counted photons. Generally, one aliquot was measured per sample, however for samples for which individual aliquots yielded a range of fading parameters (specifically samples K12, #19 and #20), several aliquots were measured.

Aliquots were heated to 100 ºC at a rate of 1 ºC/s. Four LED pulses, two seconds in length each, exposed the sample at 20 ºC, 40 ºC, 60 ºC and 80 ºC. The temperature range and LED intensity were carefully chosen to ensure that sufficient emission could be measured while preventing substantial draining. Figure 1 is representative of the raw data obtained.

Note that the intensity increased with temperature and emission occurs at 20 °C, 40 °C, 60 °C and 80 °C, coinciding with the pulsing of the LEDs.

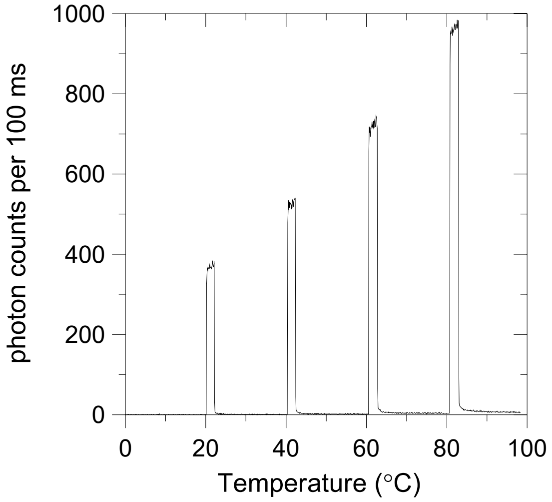

Figure 1: *Photon emission vs. temperature for K8*

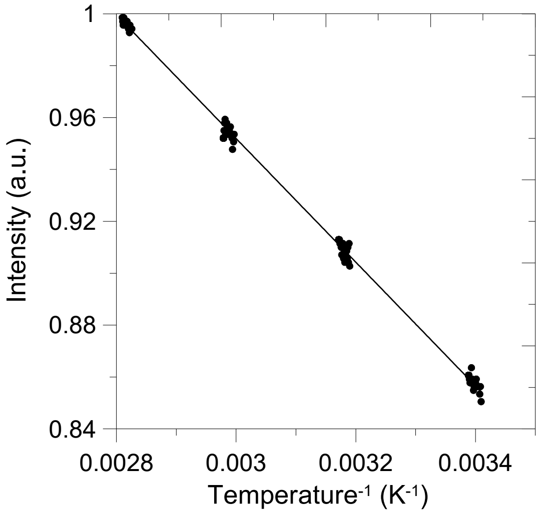

Figure 2: *Fitted data used to extract E for K8*

By fitting the data to the logarithm of equation 2,

$$\ln(I) = \ln(C) - E/kT, \quad (3)$$

E was derived. A sample fit is shown in Figure 2.

In order to get an indication of how reproducible the method was, several different CBSS aliquots were measured over three days. Figure 3 shows the calculated E values, with error bars showing the uncertainty in fitting a straight line to the data with scatter. The x-axis shows the sequence in which the samples were measured.

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[2] MDS Nordion, 447 March Road, Ottawa, ON K2K 1X8, Canada

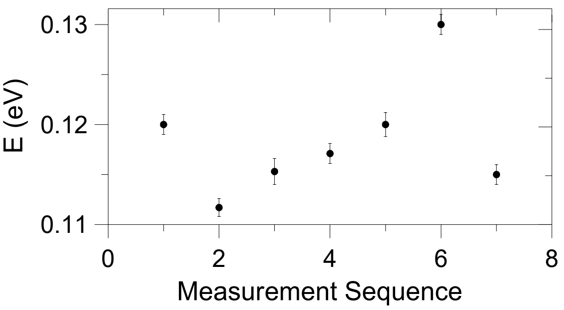

Figure 3: *Measured E values for different CBSS aliquots*

The least and greatest values measured for E differ by ~ 15 %. The first and last points in Figure 3 refer to the same aliquot, which was measured twice yielding E values that differ by less than 3 %. The standard deviation of all the E values is 5%, presumably either due to grain variability or to a lack of perfect thermal contact, in addition to that derived from fitting the data.

To determine if E was dependent on either radiation dose or annealing temperature, two additional groups of CBSS samples were measured. Aliquots of one group were bleached and then given a variety of ^{60}Co gamma cell radiation doses between 0 and 1500 Gy and then heated at 120 °C for 16 hours. The aliquots of the other group were heated at temperatures between 200 and 900 °C before radiation and heating. For both groups, E was found to be between 0.11 and 0.12 eV, thus there appears to be no dependence of the activation energy upon either radiation dose or annealing temperature.

Results

The feldspar samples tested were alkali and plagioclase feldspars, and K-feldspar grains of a particular size-range isolated from sediments. Specific feldspar samples were obtained from Ward's Natural Science, the University of Adelaide and from various individuals. Natural sediment samples were obtained from a variety of locations. Care was taken to ensure that samples represented a wide range of fading parameters. The appendix lists g and E values, in addition to mineral content information where available, for the tested samples. Figure 4 shows graphs of fading parameter versus activation energy for a) alkali feldspars, b) plagioclase feldspars and c) K-feldspar grains separated from sediments. The error bars show the uncertainty in fitting data with scatter. In Figure 4c, different symbols have been used to distinguish between K-feldspar grains separated from Canadian prairie sediments and grains separated from other sediments.

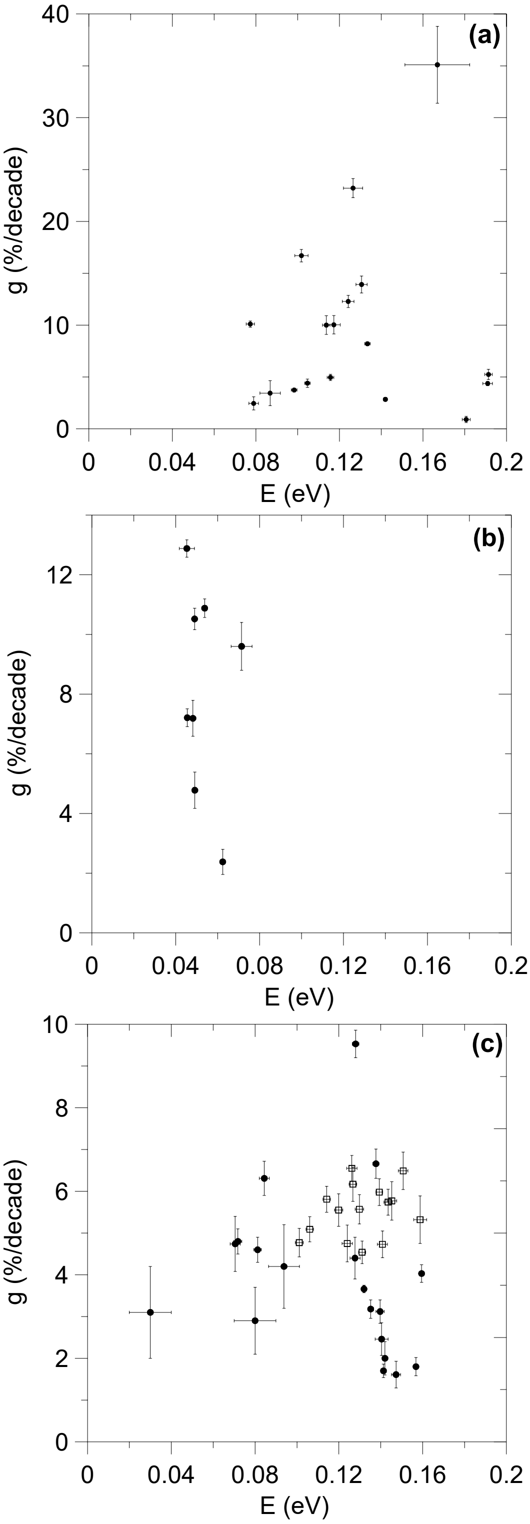

Figure 4: *Fading parameter vs. activation energy for a) alkali feldspars, b) plagioclase feldspars and c) K-feldspar grains from sediment - open squares for Canadian prairie sediments, closed circles for other sediments*

Discussion

The range of measured E values was found to be 0.03 to 0.20 eV. This range is consistent with E values reported by others, e.g. Bailiff and Poolton (1991), Duller and Wintle (1991) and Short (2003). As Figure 4 demonstrates, it would not appear wise to predict the g of a sample from a measurement of its E. However, some interesting patterns were observed. E for plagioclases lies between 0.04 and 0.07 eV whereas for alkalis, E exhibits a much wider range between 0.08 and 0.2 eV. The pattern from K-feldspar grains separated from sediments is similar to that for alkali feldspar minerals, except that the fading parameters are much lower.

Two additional concerns about the E measurement procedure are worth noting. The first, reported by Short (2003), is that the determined E will depend on the emission band measured. The second, discussed by Baril and Huntley (2003), is that the excitation spectrum changes with increasing temperature. Specifically, they reported changes in the excitation spectrum with increasing temperatures (between 290 and 490 K) for orthoclase, albite and microcline samples and thus the activation energy is different for different excitation bands; what we measured here is an average over the LED emission band.

The data were also analyzed to determine if there was any relationship between E and the contents of several major elements in the sample: K, Na, and Ca. Figure 5 shows there appears to be a positive correlation between E and K content and negative correlations with Na and Ca contents.

Conclusions

Activation energies were found for a collection of feldspars, both minerals and sediment extracts, for which fading parameters had been measured. Interesting patterns were observed, but determining the fading parameter of a sample from its activation energy would appear to be unwise. The activation energy is positively correlated to the K content and negatively correlated to Na and Ca contents.

Acknowledgements

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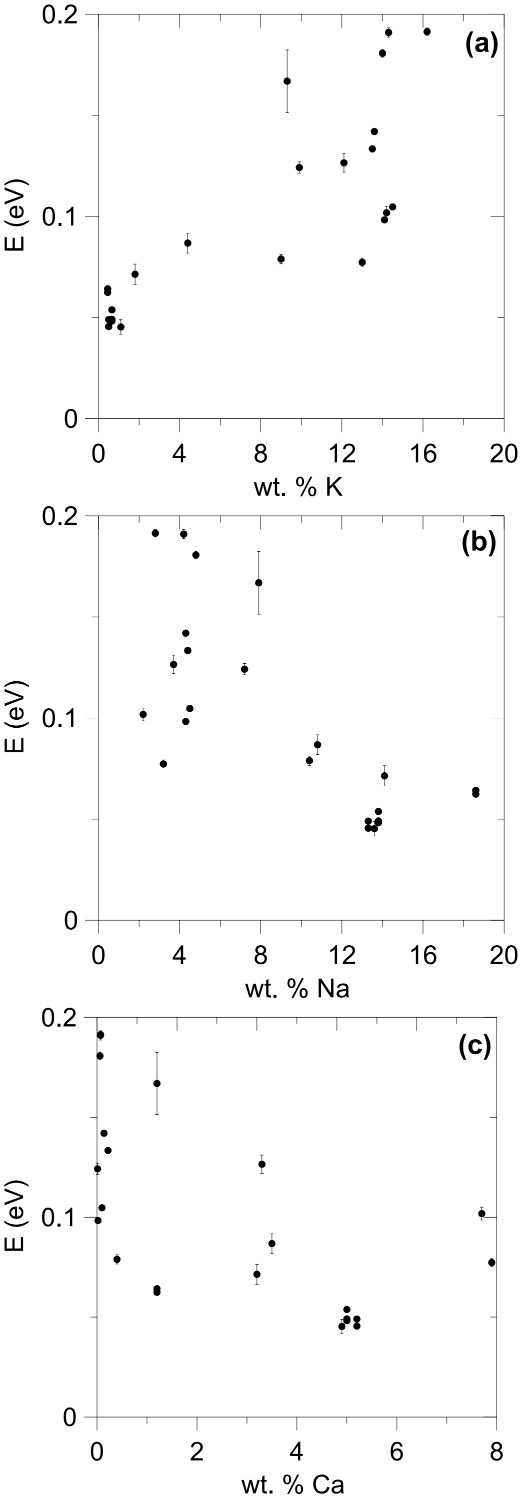

Figure 5: *Activation energy variation with major element content: a) K, b) Na, c) Ca*

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Reviewer
Ian Bailiff

Appendix: Activation energies, fading parameters and major element contents in wt. %

The feldspars are a subset of those for which fading parameters are given in Huntley and Lamothe (2001) and Huntley and Lian (in press); a fading parameter listed here is for a single aliquot and may differ from that published, which is usually an average for 5 aliquots. Values of 'g' are for t_c = 2 days after irradiation. Feldspars are from Canada unless otherwise stated. Of the 32 sediments, 22 are from Canada and the remainder are from New Zealand, the USA and Scandinavia. The three K12 results are for different crystals. The three #19 results are for slices from the same crystal; the analyses were done on a different portion of the same sample, similarly for the two #20 results.

Alkali feldspars, listed in order of decreasing K content

Sample	E (eV)	g (%/decade)	K	Na	Ca	Fe	Mg	Others > 0.01	
K13	0.191 ± 0.002	5.2 ± 0.5	16.2	2.8	0.07	0.07	0.03		microcline, Madawaska, Ontario. Ward's 46E 5124
HFC	0.105 ± 0.001	4.4 ± 0.4	14.5	4.5	0.10	0.08	0.01		perthite, Ontario
K10	0.191 ± 0.002	4.4 ± 0.2	14.3	4.2	0.07	0.04	n.d.		microcline, Keystone, S. Dakota, U.S.A Ward's #1 of 45 E 2941
K9	0.098 ± 0.001	3.7 ± 0.2	14.1	4.3	0.02	0.06	n.d.	0.04 P	microcline, var. amazonite, Kola peninsula, Murmansk, Russian Federation, Ward's #5 of 45 E 2941 & 46E 5164
K6	0.181 ± 0.002	0.9 ± 0.3	14.0	4.8	0.06	0.1	0.01	0.24 P	microcline, Ward's 45W 9252
K8	0.142 ± 0.001	2.8 ± 0.2	13.6	4.3	0.14	0.19	0.03		perthite (microcline & albite), Perth, Ontario, Ward's #4 of 45 E 2941 & 46E 0514
K3	0.133 ± 0.001	8.2 ± 0.2	13.5	4.4	0.22	0.08	n.d.	0.07 Ba	orthoclase, Red Lodge, Montana, U.S.A., U.B.C. TC313A6

K11	0.127 ± 0.005	23.4 ± 0.9	12.1	3.7	3.3	0.77	0.33	0.10 Ti, 0.18 Ba, 0.02 P, 0.03 Mn	orthoclase (Carlsbad Twin). Gothic, Colorado, U.S.A., Ward's #3 of 45 E 2941
K7	0.124 ± 0.003	12.2 ± 0.6	9.9	7.2	0.01	0.24	0.01		microcline, Crystal Peak, Colorado, U.S.A Ward's #2 of 45E 2941
PLTF	0.167 ± 0.016	35.1 ± 3.7	9.3	7.9	1.2	0.59	0.21	0.11 Ti, 0.14 Ba, 0.05 P, 0.02 Mn	Puy de la Tache, France
A5	0.079 ± 0.002	2.5 ± 0.6	9.0	10.4	0.40	0.26	0.05	0.03 Ba	"albite", Bancroft, Ontario, Ward's #7 of 45 E 2941
A4	0.087 ± 0.005	3.4 ± 1.2	4.4	10.8	3.5	3.3	1.65	0.74 Ti, 0.05 Ba, 0.30 P, 0.10 Mn	anorthoclase, Larvik, Norway, Ward's #6 of 45 E 2941
K12	0.116 ± 0.002	5.0 ± 0.3	-	-	-	-	-		orthoclase, India, Ward's 49E 5919
K12	0.131 ± 0.003	13.9 ± 0.8	-	-	-	-	-		orthoclase, India, Ward's 49E 5919
K12	0.117 ± 0.003	10.0 ± 0.9	-	-	-	-	-		orthoclase, India, Ward's 49^{E} 5919

Plagioclase feldspars, listed in order of increasing Ca content

Sample	E (eV)	g (%/decade)	K	Na	Ca	Fe	Mg	Others > 0.01	
P18	0.062 ± 0.001	2.4 ± 0.4	0.45	18.6	1.2	0.01	n.d.	0.05 Ba	oligoclase, Virginia, U.S.A.
#17	0.071 ± 0.005	9.6 ± 0.8	1.8	14.1	3.2	0.61	0.2	0.03 Ti	oligoclase, Arendal, Norway
#18	0.045 ± 0.004	12.9 ± 0.3	1.1	13.6	4.9	0.19	0.02		oligoclase, Sweden
#19	0.054 ± 0.001	10.9 ± 0.3	0.66	13.8	5	0.05	0.03		oligoclase, Renfrew County,
#19	0.048 ± 0.001	7.2 ± 0.6	"	"	"	"	"		"
#19	0.049 ± 0.001	4.8 ± 0.1	"	"	"	"	"		"
#20	0.046 ± 0.001	7.2 ± 0.3	0.5	13.3	5.2	0.15	0.01		oligoclase, Mitchell County, N. Carolina, U.S.A.
#20	0.049 ± 0.001	10.5 ± 0.4	"	"	"	"	"		"

Other minerals

Sample	E (eV)	g (%/decade)	K	Na	Ca	Fe	Mg	Others > 0.01	
BRS	0.102 ± 0.003	16.7 ± 0.6	14.2	2.2	7.7	0.29	0.09	0.04 Ti, 0.30 Ba, 0.02 Mn	sanidine Kettle Valley, B.C., contains fluorite
WCRS	0.077 ± 0.002	10.1 ± 0.3	13	3.2	7.9	0.37	0.12	0.04 Ti, 0.30 Ba, 0.03 Mn	sanidine, Kettle Valley, B.C. , contains fluorite
MCG	0.053 ± 0.007	1.0 ± 0.4	-	-	-	-	-		granodiorite, McKay Cr., North Vancouver, B.C.
CCF	0.1137 ± 0.002	10.0 ± 0.9	-	-	-	-	-		

K-feldspar separated from sediments

Canadian prairie sediments

Sample	E (eV)	g (%/decade)
SAW01-07	0.127 ± 0.002	6.2 ± 0.4
SAW01-20	0.139 ± 0.002	6.0 ± 0.3
SAW01-21	0.144 ± 0.002	5.7 ± 0.3
SAW01-22	0.145 ± 0.002	5.8 ± 0.5
SAW01-25	0.151 ± 0.002	6.5 ± 0.5
SAW01-27	0.126 ± 0.003	6.6 ± 0.3
SAW01-28	0.159 ± 0.003	5.3 ± 0.6
SAW02-01	0.120 ± 0.002	5.6 ± 0.4
SAW02-04	0.101 ± 0.002	4.8 ± 0.3
SAW02-06	0.124 ± 0.003	4.8 ± 0.4
SAW02-10	0.131 ± 0.002	4.5 ± 0.3
SAW02-13	0.141 ± 0.002	4.7 ± 0.3
SAW02-14	0.130 ± 0.002	5.6 ± 0.4
SAW02-15	0.114 ± 0.002	5.8 ± 0.3
SAW03-02	0.071 ± 0.002	4.7 ± 0.7
SAW97-12	0.106 ± 0.002	5.1 ± 0.3

Other sediments

From Canada (1-6), the U.S.A. (7-8), Scandinavia (9-10) and New Zealand (11-16)

	Sample	E (eV)	g (%/decade)
1	CCLI	0.072 ± 0.002	4.8 ± 0.3
2	BLRL2	0.081 ± 0.002	4.6 ± 0.3
3	TML1	0.132 ± 0.001	3.7 ± 0.1
4	TAG11	0.140 ± 0.003	2.5 ± 0.4
5	SAW94-62	0.084 ± 0.002	6.3 ± 0.4
6	BUCT	0.138 ± 0.002	6.7 ± 0.4
7	SN45	0.135 ± 0.001	3.2 ± 0.2
8	GP10	0.160 ± 0.001	4.0 ± 0.2
9	HJN4	0.142 ± 0.001	2.0 ± 0.4
10	HJR4	0.157 ± 0.001	1.8 ± 0.2
11	CKDS	0.140 ± 0.002	3.1 ± 0.3
12	RHIS	0.141 ± 0.001	1.7 ± 0.2
13	OTP10	0.128 ± 0.002	4.4 ± 0.5
14	PRI1	0.030 ± 0.010	3.1 ± 1.1
15	GBDS4	0.080 ± 0.010	2.9 ± 0.8
16	HBTSI	0.094 ± 0.007	4.2 ± 1.0