

**Supplementary material for:**

**Komatiites Constrain Molybdenum Isotope Composition of the Earth's Mantle**

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## **1. Samples**

### **1.1. Komati and Weltevreden Formations, Barberton greenstone belt**

The Barberton greenstone belt is located in the Kaapvaal Craton of South Africa, one of the best-preserved and studied Archean cratons. The first sample set comes from the 3.48 Ga Lower Komati Formation. The six samples analyzed are from 5 different lava flows and represent the same sample powder aliquots used by Puchtel et al. (2013) and Puchtel et al. (2014), thus they are geochemically and petrologically well characterized. The metamorphic grade of these samples did not exceed greenschist facies (Puchtel et al., 2013). Sample BV02 is from the chilled margin of a lava flow, while the others (BV01, BV03, BV10, BV13, and BV15) are all olivine cumulates with up to 60% magmatic olivine still preserved. These samples have classic Barberton-type  $\text{Al}_2\text{O}_3/\text{TiO}_2$  ratios of around 10 and  $\text{CaO}/\text{Al}_2\text{O}_3$  ratios of ca. 1.6. The primitive mantle-normalized REE abundance patterns show slight enrichments in light REE and strong depletions in heavy REE (Puchtel et al., 2013).

Two other komatiite samples were collected ~4.5km ENE of the village Tjakastad in the Barberton Greenstone Belt. Based on the map of Dann (2000), they belong to a komatiite flow of the Upper Komati Formation. The Tjakastad sequence has been strongly recrystallized under the greenschist facies conditions. Petrographic and XRD study revealed a mineral assemblage dominated by actinolite and chlorite with minor amounts of albite and iron oxides. No chromite is visible in thin sections and none were left over after the chemical treatment, which contrasts with the much less altered samples from the other locations. The spinifex textures are still well preserved in both samples.

The eight samples from the 3.26 Ga Weltevreden Formation were collected from three different flows and are either olivine cumulates (501-1, 501-8, 427-5 and 12-7) or olivine spinifex-textured lavas (501-3, 564-4, 564-5, and 12-2; see Puchtel et al., 2013). Studies concentrated on the metamorphism and alteration of these rocks showed that the best-preserved layers have olivine crystals with unaltered melt inclusions, an indication that these komatiites are remarkably well preserved (Kareem, 2005; Connolly et al., 2011). The  $\text{Al}_2\text{O}_3/\text{TiO}_2$  ratios are high with values around 30 and the  $\text{CaO}/\text{Al}_2\text{O}_3$  ratios are low with values around 0.6, indicating that these lavas belong to the Al-enriched type (Connolly et al., 2011). The primitive mantle-normalized REE patterns show depletions in light REE and enrichments in heavy REE (Puchtel et al., 2013).

### **1.2. Pyke Hill locality, Abitibi greenstone belt**

The Pyke Hill area is located in Munro Township in Canada. The samples were collected from two differentiated lava flows, PH-I and PH-II. The geochemical and petrographic characterization of the samples is given in Puchtel et al. (2004a) and Puchtel et al. (2004b). Samples PH13, PH14, PH26 and PH27 are random olivine-spinifex textured rocks, whereas samples PH31 and PH33 are olivine cumulates. Their age of about 2.7 Ga has been determined using the Sm-Nd and Pb-Pb methods on bulk rocks and U-Th dating on zircons (Dupré et al., 1984, Lahaye and Arndt 1996, Carignan et al., 1995). The Pyke Hill komatiites belong to the Munro type lavas with  $\text{Al}_2\text{O}_3/\text{TiO}_2 \sim 20$  and  $\text{CaO}/\text{Al}_2\text{O}_3 \sim 1$ . The primitive mantle normalized REE patterns show depletions in light REE and essentially flat heavy REE abundances (Puchtel et al., 2004b).

### 1.3. Victoria's Lava Lake, Vetreny belt

Komatiites from the 2.41 Ga Victoria's Lava Lake in Vetreny Belt (Russia) are the youngest samples analyzed in this study. Seven samples from this location have been measured for their Mo concentrations and isotope compositions, including one flowtop breccia (sample 01110/1), one upper chilled margin (sample 01111), one random plate olivine spinifex (sample 91101), one basalt (12124) and three olivine cumulates (01001\_A, 01105, 12106). The samples have been collected in different years but from the same outcrops as described in Puchtel et al., (1996) and Puchtel et al., (2001). Thus, sample 01110/1 corresponds to 91110, 01111 to 91112, 01001\_A to 91105/1, 01105 to 91105, 12124 to 91124 (Figure 2 in Puchtel et al., 1996) and 12106 to 91106 (Figure 1 in Puchtel et al., 2001). All these samples were collected from a single differentiation pond of komatiitic lava. Except for the flowtop breccia and the upper chilled margin samples, the rocks represent almost completely unaltered mineral assemblages (Puchtel et al., 1996). Geochemical and isotopic studies have shown that the original komatiite magma was contaminated with ca. 8% of upper crustal material *en route* to the surface (Puchtel et al., 1996, Puchtel et al., 1997). Detailed petrographic description of the rocks can be found in Puchtel et al. (1996). The komatiites from Victoria's Lava Lake have  $\text{Al}_2\text{O}_3/\text{TiO}_2 \sim 20$  and  $\text{CaO}/\text{Al}_2\text{O}_3 \sim 0.8$ , which are both close to the chondritic values. The REE patterns show enrichment in LREE, which was interpreted to be the result of contamination of the primary magma with upper crustal rocks (Puchtel et al., 1996, Puchtel et al., 1997). To evaluate the effects of crustal contamination, two tonalites (K04, K13) from the early Archean Vodla Block, flanking the komatiite containing greenstone belt southeasterly, have been analyzed for their Mo concentrations and isotopic compositions.

## 2. Blank/Sample ratios

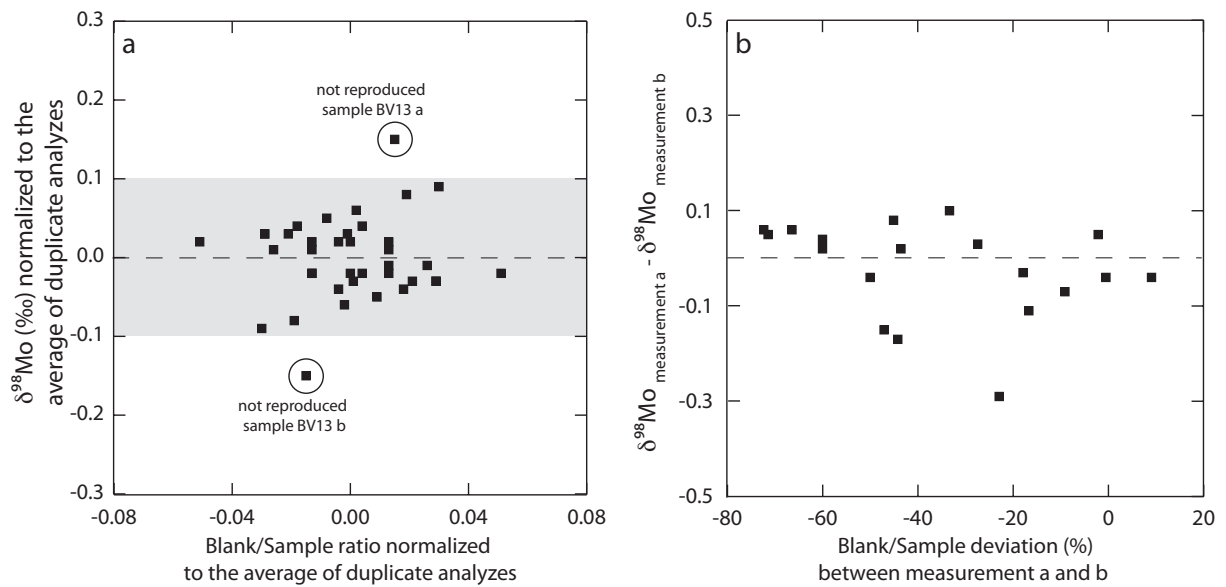


Figure S1: a) Illustrates the blank/sample ratio versus the Mo isotope composition of samples measured in duplicate, both normalized to their average value. No correlation can be found that would suggest that higher blank contributions affect the  $\delta^{98}\text{Mo}$  uniformly and significantly. All data except sample BV13 plot within the  $\pm 0.1\text{‰}$  reproducibility of the reference material (2SD). b) Difference between the  $\delta^{98}\text{Mo}$  of duplicate analyses versus the difference in the blank/sample ratio (given in percent) between the two measurements. No correlation between the difference in the  $\delta^{98}\text{Mo}$  and the blank/sample ratio is found, indicating that the blank did not significantly affect the measured Mo isotope compositions.

### 3. Ruthenium correction of Mo isotope data

The  $^{98}\text{Ru}$  and  $^{100}\text{Ru}$  interference have been calculated and subtracted from the affected Mo isotope individually for each cycle the following:

$${}^x\text{Ru} = {}^{99}\text{Ru}_{\text{measured}} \cdot \text{NAR}_{x\text{Ru}/99\text{Ru}} \cdot \left( \frac{m_{x\text{Ru}}}{m_{99\text{Ru}}} \right)^F \quad (1)$$

with:

$x\text{Ru} = {}^{98}\text{Ru}$  or  $^{100}\text{Ru}$

NAR = natural abundance ratio

F = ICP fractionation factor, taken from the double spike data reduction without Ru correction

m = mass of isotope

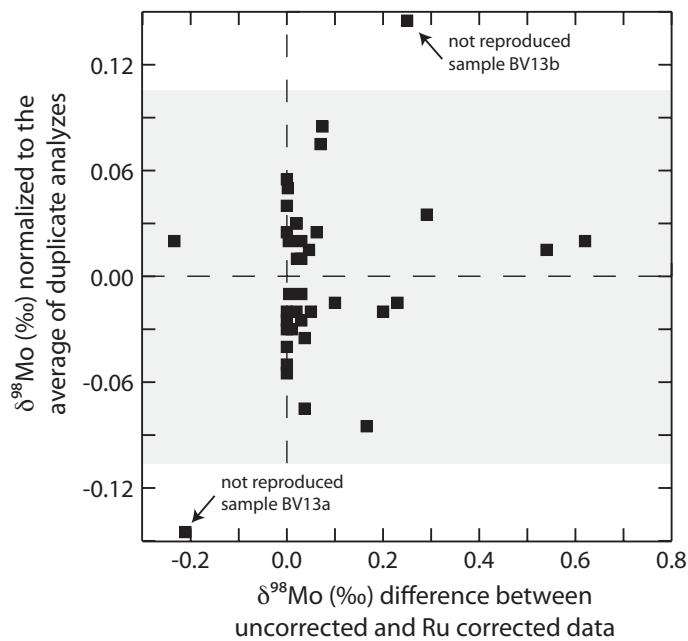


Figure S2: Shows the degree of  $\delta^{98}\text{Mo}$  correction due to Ru interference (horizontal axis) relative to the deviation of duplicates “a” and “b” normalized to their average value (vertical axis). Samples that suffered low or no Ru correction do not reproduce better than samples with strong Ru correction. In addition, duplicated samples where analyses “a” and analyses “b” were subjected to different degrees of Ru correction (see e.g. PH31, PH33 and BV15 in Table S3) show good reproducibility. This indicates robustness of the applied Ru correction. Grey shaded area represents  $\pm 0.1\text{‰}$  (2SD) reproducibility of reference material.

Table S1: Uncorrected and Ru corrected  $\delta^{98}\text{Mo}$  data, average  $^{99}\text{Ru}$  signal and average  $^{99}\text{Ru}/^{95}\text{Mo}$ .

Sample	$\delta^{98}\text{Mo}$ ‰ uncorrected	$^{99}\text{Ru}$ (V)	$^{99}\text{Ru}/^{95}\text{Mo}$	$\delta^{98}\text{Mo}$ ‰ corrected	Mo unc - Mo corr
01110/1 a	0.09	2.57E-05	1.22E-04	<b>0.09</b>	0.00
01110/1 b	0.17	2.49E-05	8.02E-05	<b>0.17</b>	0.00
01111 a	0.30	3.04E-05	1.94E-04	<b>0.29</b>	0.01
01111 b	0.37	8.84E-05	1.95E-04	<b>0.35</b>	0.02
91101 a	0.17	5.05E-06	2.98E-05	<b>0.17</b>	0.00
91101 b	0.25	9.65E-07	2.89E-06	<b>0.23</b>	0.02
01001_A	0.27	2.94E-04	6.29E-04	<b>0.25</b>	0.02
1105 a	0.16	1.88E-04	7.75E-04	<b>0.13</b>	0.03
1105 b	0.18	6.01E-04	1.35E-03	<b>0.15</b>	0.03
12124 a	0.16	2.51E-06	2.55E-06	<b>0.16</b>	0.00
12124 b	0.05	-6.09E-06	-7.09E-06	<b>0.05</b>	0.00
12106 a	0.01	6.87E-05	1.78E-04	<b>0.01</b>	0.00
12106 b	0.11	6.61E-05	2.02E-04	<b>0.11</b>	0.00
K04 a	0.21	1.30E-05	4.58E-05	<b>0.21</b>	0.00
K04 b	0.25	2.50E-05	1.17E-04	<b>0.25</b>	0.00
K13 a	-0.10	-2.14E-06	-6.37E-06	<b>-0.10</b>	0.00
K13 b	-0.05	-5.53E-06	-1.84E-05	<b>-0.05</b>	0.00
PH13 a	0.02	2.44E-03	7.07E-03	<b>0.01</b>	0.01
PH13 b	0.05	3.58E-04	1.18E-03	<b>0.03</b>	0.02
PH14	0.14	5.29E-04	1.31E-03	<b>0.10</b>	0.04
PH26	0.21	1.00E-03	4.26E-03	<b>0.04</b>	0.17
PH27	0.29	1.02E-03	4.50E-03	<b>0.06</b>	0.23
PH29 a	0.29	2.84E-03	1.51E-02	<b>-0.03</b>	0.29
PH29 b	-0.06	4.02E-04	1.43E-03	<b>-0.10</b>	0.04
PH31 a	0.81	2.68E-03	1.47E-02	<b>0.19</b>	0.62
PH31 b	0.35	1.34E-03	5.90E-03	<b>0.15</b>	0.20
PH33 a	-0.22	2.25E-03	1.22E-02	<b>0.01</b>	-0.23
PH33 b	0.02	3.31E-04	1.20E-03	<b>-0.03</b>	0.05
501-1	1.22	1.41E-02	3.54E-02	<b>0.02</b>	1.20
501-3	0.16	1.57E-03	4.08E-03	<b>0.06</b>	0.10
501-8	0.76	1.10E-02	2.89E-02	<b>0.13</b>	0.63
427-5	0.58	1.37E-02	3.36E-02	<b>-0.04</b>	0.62
564-4	0.47	1.34E-03	7.21E-03	<b>0.07</b>	0.40
564-5 a	0.16	1.55E-03	6.18E-03	<b>0.09</b>	0.07
564-5 b	0.09	1.03E-03	3.44E-03	<b>-0.08</b>	0.17
12-2	0.30	4.86E-03	1.40E-02	<b>0.10</b>	0.20
12-7	0.63	1.57E-02	3.62E-02	<b>-0.03</b>	0.66
BV01 a	0.44	6.89E-04	1.85E-03	<b>0.37</b>	0.07
BV01 b	0.26	1.01E-03	2.19E-03	<b>0.22</b>	0.04
BV02 a	0.11	1.88E-04	6.04E-04	<b>0.08</b>	0.03
BV02 b	0.19	2.36E-03	5.28E-03	<b>0.13</b>	0.06
BV03	0.60	9.67E-04	2.44E-03	<b>0.54</b>	0.06
BV10 a	0.48	6.23E-04	2.56E-03	<b>0.38</b>	0.10
BV10 b	0.46	7.48E-04	2.91E-03	<b>0.41</b>	0.05
<i>BV13 a<sup>A</sup></i>	<i>0.91</i>	<i>1.30E-03</i>	<i>5.41E-03</i>	<i>0.66</i>	<i>0.25</i>
<i>BV13 b<sup>A</sup></i>	<i>0.16</i>	<i>7.29E-03</i>	<i>1.90E-02</i>	<i>0.37</i>	<i>-0.21</i>
BV15 a	1.25	2.55E-03	1.07E-02	<b>0.71</b>	0.54
BV15 b	0.91	8.66E-03	2.63E-02	<b>0.68</b>	0.23
Tjakastad-1 a	0.76	1.65E-04	3.82E-04	<b>0.73</b>	0.03
Tjakastad-1 b	0.71	1.65E-04	5.29E-04	<b>0.69</b>	0.02
Tjakastad-2	0.72	1.69E-04	5.65E-04	<b>0.69</b>	0.03

A:  $\delta^{98}\text{Mo}$  of sample BV13 has not been reproduced during duplicate analyses

#### 4. Additional data; Tables S2 and S3 showing major and trace element chemistry of Tjakastad samples and Mo concentration of chromites

Table S2: Major and trace element data for altered Tjakastad samples

Sample	Tjakastad-1	Tjakastad-2
SiO <sub>2</sub> (wt%)	55.87	53.81
TiO <sub>2</sub>	0.59	0.57
Al <sub>2</sub> O <sub>3</sub>	9.39	9.69
Fe <sub>2</sub> O <sub>3</sub>	9.41	10.42
MnO	0.12	0.14
MgO	12.76	13.72
CaO	8.17	8.43
Na <sub>2</sub> O	3.40	2.97
K <sub>2</sub> O	0.23	0.18
LOI	3.91	2.20
La (µg/g)	1.68	3.88
Ce	4.77	8.42
Nd	3.68	4.87
Sm	1.36	1.31
Eu	0.50	0.56
Gd	1.90	1.90
Dy	2.27	2.34
Er	1.45	1.48
Yb	1.43	1.34
(La/Sm)N	0.78	1.86
(Gd/Yb)N	1.07	1.15
Zr	36.9	34.9
Nb	1.8	1.7
Y	13.4	13.0
Cr	1157	1344
V	242	206
Ni	279	283
Sc	33.7	31.8

Concentrations recalculated on an anhydrous basis

Table S3: Chemical composition of chromites analysed with LA-ICP-MS

Sample		91105	91111	1001_A	12-7
n		11	11	12	12
Location		Victoria's Lava Lake			Weltevreden
MgO (25)	wt%	3.6	0.5	3.1	12.4
Al <sub>2</sub> O <sub>3</sub> (27)	wt%	16.5	15.9	16.4	8.8
TiO <sub>2</sub> (49)	wt%	0.4	0.4	0.4	0.2
Cr <sub>2</sub> O <sub>3</sub> (53)	wt%	47.2	48.5	47.8	62.1
MnO (55)	wt%	0.4	0.9	0.4	0.2
FeO (57)	wt%	31.9	33.9	32	16.4
Co (59)	µg/g	385	509	454	224
Ni (62)	µg/g	914	1090	851	1155
Mo (95)	µg/g	<0.7	≤1.6	<0.7	<0.4

Number in parentheses indicates isotope used for measurement



## 5. Rayleigh distillation lower Komati Formation

Table S4: Calculated parameters for Rayleigh distillation of lower Komati Formation komatiites.

Sample	$\delta^{98}\text{Mo}$	Mo (ng/g)	Mo loss (ng/g) <sup>A</sup>	F (Mo lost)	$\Delta^{98}\text{Mo}$ (‰) <sup>B</sup>
BV02	0.11	51	0	0	-
BV01	0.29	29	13	0.31	-0.41
BV03	0.54	17	20	0.54	-0.43
BV10	0.40	21	16	0.43	-0.41
BV13	0.57	15	22	0.60	-0.38
BV15	0.69	13	24	0.65	-0.40

A: Mo deviation between sample and inferred olivine control line through sample BV02 and MgO concentration of olivine (see Figure 1A).

B:  $\Delta^{98}\text{Mo} = (\ln(\delta^{98}\text{Mo}_{\text{sample}}+1) - \ln(\delta^{98}\text{Mo}_{\text{BV02}}+1))/\ln(F)$ . Average is  $-0.41 \pm 0.03$  ‰ (2SD).

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