

## NOTE

# New supplemental activator for lead isotope analysis using TIMS

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We have devised a new supplementary activator for lead isotope measurements performed using thermal ionization mass spectrometry (TIMS). The activator consisted of a mixture of 250 ppm Ge and 500 ppm Re and was used with normal colloidal silica. This new substance shows excellent performance in terms of enhancing the ion beam intensity. The supplementary activator yielded  $3.5\text{--}4.5 \times 10^{-11}$  A  $^{208}\text{Pb}$  for 10 ng Pb,  $1.5\text{--}2.5 \times 10^{-11}$  A for 5 ng Pb, and  $\sim 1.5 \times 10^{-11}$  A for 2.5 ng Pb samples, indicating that the new activator was superior to those currently in use. This improvement should be applicable to samples with low Pb content, for example, in environmental tracer studies and Pb–Pb chronology studies.

Keywords: Pb isotope, activator, TIMS, colloidal silica, germanium

## INTRODUCTION

The development of multi-collector-inductively coupled plasma-mass spectrometry (MC-ICP-MS) has enabled measurement of the isotopic compositions of many elements (Yang, 2009). For elements such as Sr, Nd, and Pb, which are accompanied by radiogenic isotopes and are widely applied in the field of isotope geochemistry, MC-ICP-MS enables their precise determination of isotopic ratios provided that an appropriate amount of sample (e.g., 5–10 ng) is available for analysis. It may therefore be relevant to question whether the development of MC-ICP-MS spells the end of thermal ionization mass spectrometry (TIMS) in scientific investigations. However, as shown by recent studies that used TIMS to measure the isotopes of sub-nanogram size of Sr, Nd and Pb (Amelin and Davis, 2006; Chu *et al.*, 2009; Harvey and Baxter, 2009), TIMS remains an important tool to precisely determine the isotopic composition of small samples.

In the case of Pb, the analytical precision of measured isotope ratios is several times worse than those for Sr and Nd, because only one non-radiogenic isotope,  $^{204}\text{Pb}$ , is available among the four stable isotopes. Therefore, (1) no isotopic ratio is available for internal normalization,

and (2)  $^{204}\text{Pb}$  is used as the denominator for lead isotope ratios ( $^{206}\text{Pb}/^{204}\text{Pb}$ ,  $^{207}\text{Pb}/^{204}\text{Pb}$ , and  $^{208}\text{Pb}/^{204}\text{Pb}$ ), although its low abundance results in poor reproducibility, especially in the case of small samples. This disadvantage can be overcome by using the double-spike (DS) method (Dodson, 1963; Compston and Oversby, 1969). However, duplicate analysis of a single sample requires a long period of data acquisition using single-collector TIMS. This limitation has largely been overcome by the development of multi-collector TIMS, which has drastically reduced the measurement time (Hamelin *et al.*, 1985; Woodhead *et al.*, 1995). A remaining challenge is to optimize the ionization efficiency of Pb when using the DS method, as this would extend the lower limits of sample volume necessary for Pb isotope measurements.

The use of a silica-gel activator with phosphoric acid results in the enhanced Pb ion beam intensity (Cameron *et al.*, 1969) and is effective in terms of limiting instrumental mass fractionation during analysis. Gerstenberger and Haase (1997) reported a stable  $^{208}\text{Pb}$  ion beam of  $3\text{--}4 \times 10^{-11}$  A for 10 ng Pb of the NBS standard using suspended colloidal silica. Kuritani and Nakamura (2002) obtained  $2\text{--}3 \times 10^{-11}$  A of  $^{208}\text{Pb}$  for  $\sim 10$  ng Pb,  $1\text{--}2 \times 10^{-11}$  A for  $\sim 5$  ng, and  $0.4\text{--}0.6 \times 10^{-11}$  A for  $\sim 1$  ng. Nohda (1999) and Kani and Nohda (2002) proposed a method using fused silica-gel to obtain a stable Pb ion beam with TIMS; however, sample sizes needed were larger than 100 ng, unsuitable for analyses of low abundance natural samples.

The aim of the present study is to enhance Pb ion beam intensity and to develop a method for measuring Pb iso-

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topes in low abundance natural specimens. To this end, we propose a new supplementary activator composed of 250 ppm Ge and 500 ppm Re, in addition to colloidal silica, and discuss its ionization behavior and efficiency.

## EXPERIMENTS

### Colloidal silica

Colloidal silica with phosphoric acid is indispensable as an activator in Pb isotope analysis techniques (Cameron *et al.*, 1969). The ionization efficiency depends on the quality and quantity of colloidal silica, the density of phosphoric acid, and their mixing ratio. In particular, the grain size of the colloidal silica is important in this regard (Gerstenberger and Haase, 1997). To replace the silicic acid-colloidal solution used by Gerstenberger and Haase (1997), Miyazaki *et al.* (2005) tested a colloidal silica product by the Nissan Chemical Industries Ltd. We followed their work using the same material, and tried other materials produced by Nissan Chemicals (e.g., SNOWTEX-AK, grain size 10~20 nm; -PSS, grain size 80~120 nm). The results of several tests revealed that the finest grains of colloidal silica, SNOWTEX-OXS (10.7% SiO<sub>2</sub>, grain size 4~6 nm), yielded the best performance in terms of obtaining a high Pb ion beam intensity. Because the material contained various concentrations of many elements in addition to Pb (5.6 ppb), impurities were eliminated by ion exchange (AG 50W × 12). OXS was then diluted and adjusted to 1000 ppm SiO<sub>2</sub> in 0.1N-H<sub>3</sub>PO<sub>4</sub> solution. At the time, the loading blank from the colloidal silica was estimated to be less than 0.1 pg.

### Supplementary activator

The use of colloidal silica OXS yields a high Pb ion beam intensity; however, the use of Pb with colloidal silica activator produces this high beam intensity only for a short period of time. Following the successful use of an Al activator for Cr isotope analysis using TIMS (Trinquier *et al.*, 2008), we tried to search the Group 14 elements for additional metal ions as an emitter for Pb, and found that Ge addition is effective in enhancing the Pb ion beam intensity. In addition to Ge, the Re oxide was expected to activate Pb ionization from analogy with Ta<sub>2</sub>O<sub>5</sub> in the case of Nd isotope analysis (Harvey and Baxter, 2009). Actually, it also showed that the lifetime of the Pb ion beam could be prolonged by additional Re doping. We utilized Ge and Re in 2% HNO<sub>3</sub> solution distributed by High Purity Standard. Therefore, an optimum proportion among the colloidal silica, phosphoric acid, Ge and Re (herein referred to as GR) were examined in this study.

### Sample loading

The Pb sample was mixed with 1 μl colloidal silica (1000 ppm SiO<sub>2</sub> in 0.1 N H<sub>3</sub>PO<sub>4</sub>) and 1 μl GR, then loaded

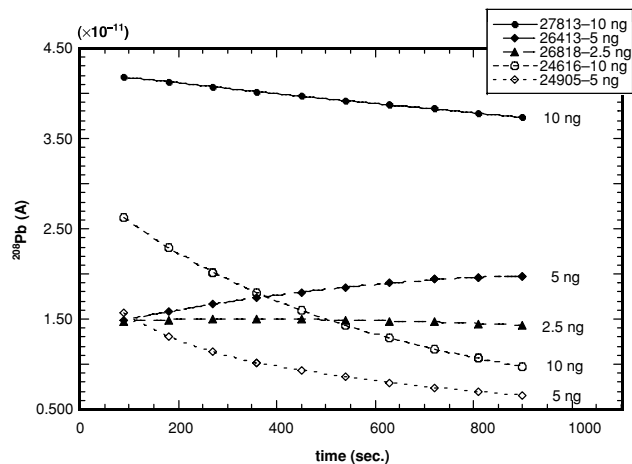


Fig. 1. Pb ion beam intensities for 2.5 ng Pb, 5.0 ng Pb, and 10 ng Pb samples. Filled marks (circles, diamonds and triangles) indicate measurements using the GR additive; Open marks (circles and diamonds) indicate measurements without the use of GR.

onto a single V-shaped Re filament. After the solution had been loaded, the electric current passing through the filament was slowly increased to 1.5 A and was maintained at this current for 60 sec before being reduced to zero. The filament was then heated by applying an electric current of 3.2 A for 1.5 sec, controlled by a timer (Nohda, 1999; Kani and Nohda, 2002). Instantaneous heating to high temperatures appeared to have perfectly fused the colloidal silica on the filament to the glass, and almost all H<sub>3</sub>PO<sub>4</sub> was evaporated. At this point, doped Re and Ge were probably present as an oxides. The total blank was estimated to be less than 30 pg.

### TIMS

All Pb isotopic compositions were determined using a Thermo Fisher Scientific TRITON instrument at National Cheng Kung University (NCKU). Ion beams for the four isotopes were measured in static multi-collector mode using four Faraday cups with 10<sup>11</sup> Ω feedback resistors. Gain calibration was conducted at least once per day following the standard operation procedures. Each measurement run consisted of 200 ratios in 10 blocks of 15 min.

### Test at University of the Ryukyus

The supplementary activator, GR, was independently assessed by Shinjo at University of the Ryukyus (UR) to confirm its efficiency. In these analyses, 2.5, 5, and 10 ng NIST SRM 981 Pb samples were loaded onto a Re filament with GR and the colloidal silica prepared at NCKU. Besides them, tests without GR supplementary activator were also conducted on the samples of 10, 50,

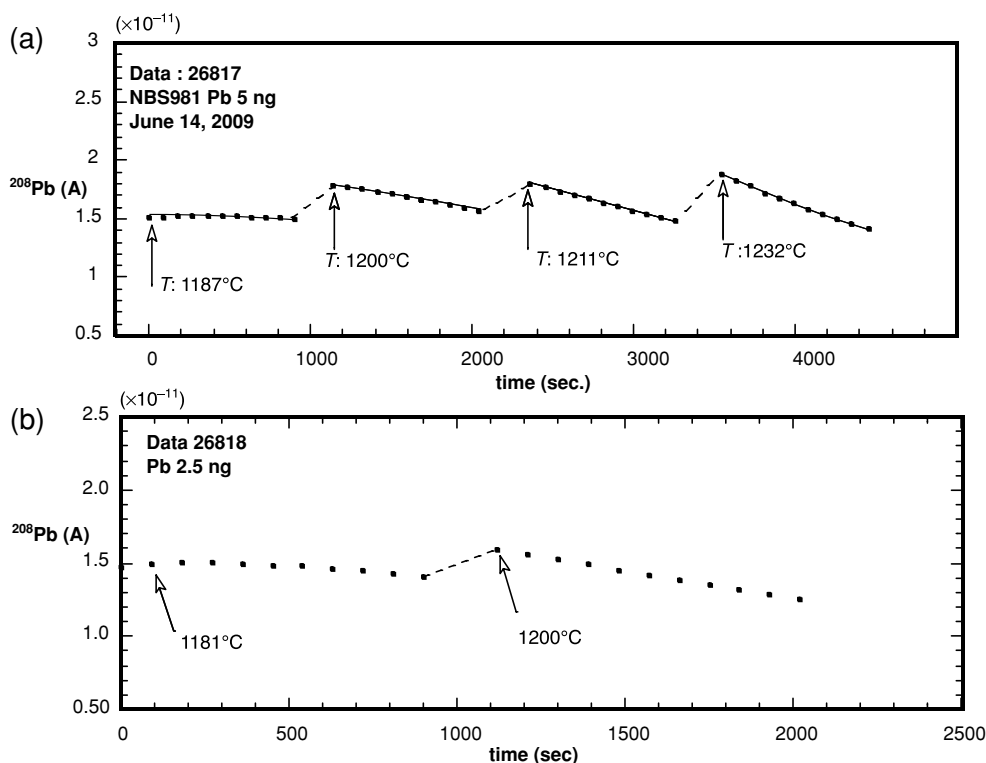


Fig. 2. Ion beam durations for (a) 5.0 ng and (b) 2.5 ng Pb samples with GR.

and 100 ng using the colloidal silica utilized at UR. Each measurement run consisted of 40 ratios in 4 blocks and the total measurement time for one sample was 11 minutes.

## RESULTS AND DISCUSSION

### Effect of GR

Figure 1 shows the Pb ion beam intensities for the case of GR additions to 10, 5, and 2.5 ng Pb samples, and for the case of no GR addition to the 10 or 5 ng Pb samples. GR addition effectively enhanced the Pb ion beam intensity, although it is not certain that the mixing ratio of Ge to Re used here was optimal. We subsequently performed a series of tests in which the added quantity of Ge was varied, keeping the quantity of Re fixed at 500 ng. The Pb ion beam was strong and stable for Ge additions between 250 ng and 2  $\mu\text{g}$ , but the intensity gradually decreased and the beam became unstable at Ge additions between 2 and 16  $\mu\text{g}$ . The filament with 16  $\mu\text{g}$  Ge addition yielded highly unstable ion beam and decayed rapidly. It seems to be owing to matrix effect by Ge. Accordingly, a stable, strong ion beam was obtained for Ge additions of 250–2000 ng. Similarly, Re addition tests with 500 to 1500 ng showed no remarkable changes in the Pb ion beam intensity or durability. Thus, the optimal con-

Table 1. Ion yield

Data file	Pb amount (ng)	$^{208}\text{Pb}$ ( $\times 10^{-11}$ A)	Sampling time (min)	GR	Ion yield (%)
27813	10	3.95	15	○	1.46
24616	10	1.21	15	×	0.45
26413	5	1.79	15	○	1.32
26817	5	1.62	60	○	4.79
24905	5	0.4	15	×	0.3
26818	2.5	1.62	15	○	4.28

centration at 250 ng Ge and 500 ng Re (GR) was employed in the present study.

As shown in Fig. 1, 10 ng Pb with GR gave stable and strong ion beam intensity which can be correlated with those of Gerstenberger and Haase (1997). In the case of 5 ng Pb (26413), we obtained increasing ion beam of  $^{208}\text{Pb}$  from 1.5 to  $2.0 \times 10^{-11}$  A. Another 5 ng Pb (26817) showed from 1.5 to  $2.0 \times 10^{-11}$  A with increasing filament temperature over 60 min (Fig. 2a). A  $^{208}\text{Pb}$  ion beam intensity of  $1.5 \times 10^{-11}$  A for 2.5 ng Pb (26818) was observed over 30 min (Fig. 2b). In evaluating effect of GR, we calculated the ion yield which is defined as the numbers of registered by the collectors divided by the number of atoms used for analysis (Chu *et al.*, 2009). As shown in

Table 2. Pb isotope ratios of NIST SRM-981

	$^{206}\text{Pb}/^{204}\text{Pb}$	2SE	$^{207}\text{Pb}/^{204}\text{Pb}$	2SE	$^{208}\text{Pb}/^{204}\text{Pb}$	2SE	$^{208}\text{Pb}$ (V) at ACQ start	$^{208}\text{Pb}$ (V) at ACQ finish	Decay rate (%)
With colloidal silica of RU									
100 ng	16.9416	0.0015	15.4987	0.0013	36.7218	0.0033	2.089	2.092	(0.1)
50 ng	16.9422	0.0016	15.4993	0.0015	36.7235	0.0037	2.174	1.853	14.8
10 ng	16.9417	0.0018	15.4969	0.0018	36.7173	0.0047	2.343	1.735	26.0
RU ave. $\pm 2\text{SD}$	16.9418	0.0006	15.4983	0.0025	36.7209	0.0064			
Sample A									
Pb 10 ng with OXS colloidal silica and GR									
A1	16.9436	0.0013	15.5011	0.0013	36.7277	0.0031	2.469	2.251	8.8
A2	16.9450	0.0010	15.5026	0.0010	36.7316	0.0022	2.450	2.176	11.2
A3	16.9414	0.0012	15.4982	0.0011	36.7204	0.0024	2.521	2.238	11.2
A4	16.9406	0.0011	15.4974	0.0011	36.7184	0.0024	2.581	2.304	10.7
A5	16.9411	0.0018	15.4968	0.0016	36.7171	0.0038	2.451	2.205	10.1
average $\pm 2\text{SD}$	16.9423	0.0038	15.4992	0.0050	36.7230	0.0126			
Sample B									
Pb 5 ng with OXS colloidal silica and GR									
B1	16.9421	0.0014	15.5001	0.0012	36.7251	0.0035	2.464	2.212	10.2
B2	16.9412	0.0015	15.4986	0.0013	36.7215	0.0033	2.390	2.035	14.9
B3	16.9427	0.0013	15.4994	0.0012	36.7236	0.0028	2.463	2.085	15.4
B4	16.9400	0.0013	15.4962	0.0014	36.7154	0.0031	2.445	2.037	16.7
B5	16.9373	0.0018	15.4925	0.0016	36.7061	0.0038	2.496	2.007	19.6
average $\pm 2\text{SD}$	16.9407	0.0043	15.4974	0.0062	36.7183	0.0156			
Sample C									
Pb 2.5 ng with OXS colloidal silica and GR									
C1	16.9381	0.0025	15.4949	0.0021	36.7122	0.0053	1.210	0.895	26.0
C2	16.9414	0.0023	15.4972	0.0021	36.7181	0.0051	1.313	0.918	30.1
C3	16.9421	0.0025	15.4986	0.0024	36.7214	0.0051	1.569	1.019	35.1
C4	16.9415	0.0026	15.4956	0.0024	36.7143	0.0060	1.452	1.255	13.6
average $\pm 2\text{SD}$	16.9408	0.0036	15.4966	0.0033	36.7165	0.0082			
Grand mean $\pm 2\text{SD}$	16.9414	$\pm 0.0036$	15.4979	$\pm 0.0048$	36.7197	$\pm 0.0121$			
Published data									
Catanzaro <i>et al.</i> (1968)	16.937	0.011	15.491	0.015	36.721	0.036			
Hamelin <i>et al.</i> (1985)	16.9403	0.0057	15.4956	0.0074	36.7176	0.0211			
Woodhead <i>et al.</i> (1995)	16.937	0.004	15.492	0.005	36.708	0.013			
Todd <i>et al.</i> (1996)	16.9356	0.0023	15.4891	0.003	36.7006	0.0113			
Galer and Abouchami (1998)	16.9405	0.0015	15.4963	0.0016	36.7219	0.0044			
Fölling <i>et al.</i> (2000)	16.9305	0.0121	15.4936	0.0128	36.7119	0.0302			
Thirlwall (2000)	16.9409	0.0022	15.4956	0.0026	36.7228	0.008			
Vlastelic <i>et al.</i> (2001)	16.9409	0.0014	15.4976	0.002	36.7258	0.0059			
Bolhar <i>et al.</i> (2002)	16.938	0.001	15.496	0.006	36.701	0.016			

Decay rate (%) =  $[(^{208}\text{Pb}/^{204}\text{Pb}) \text{ at ACQ start} - (^{208}\text{Pb}/^{204}\text{Pb}) \text{ at ACQ finish}] / (^{208}\text{Pb}/^{204}\text{Pb}) \text{ at ACQ start} \times 100$ .

2SD = 2 \* Standard Deviation.

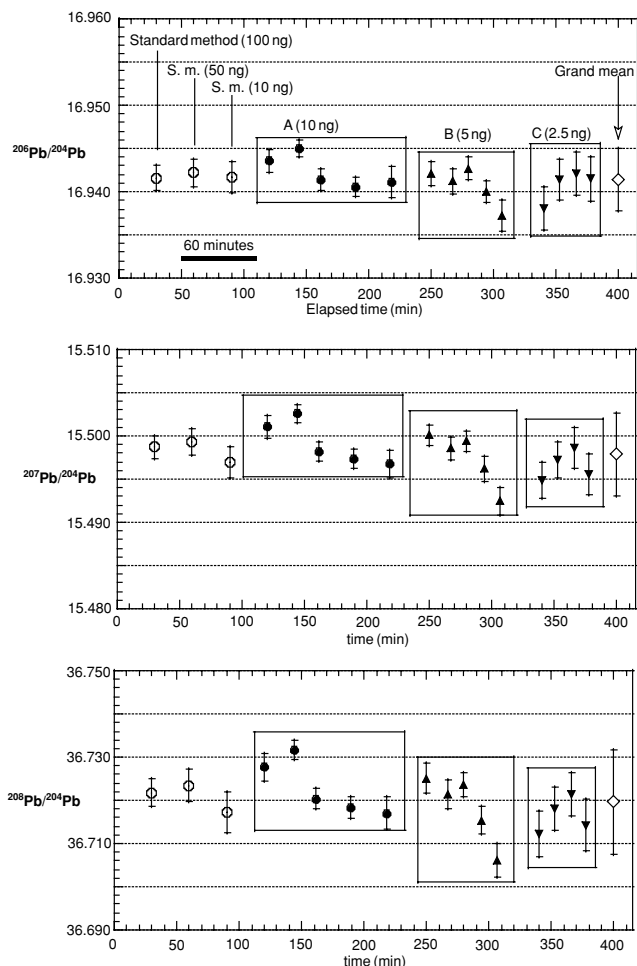


Fig. 3. Pb isotopic compositions measured at University of the Ryukyus. Data were corrected mass discrimination using the double-spiked run. The standard method included loading the Pb with the colloidal silica utilized at UR. Samples A (10 ng Pb), B (5 ng Pb), and C (2.5 ng Pb) were loaded with OXS colloidal silica and GR.

Table 1, the effect of GR is evident in comparing with the ion yield of the GR doped sample and no GR addition. As the ion yield is a function of measurement time, the present results should not be simply compared with those of reported values. However, Gerstenberger and Haase (1997) reported excellent ion yields of 9.8% and 11.6% for the strong and stable ion beam intensities ( $3$  to  $4 \times 10^{-11}$  A) with long duration ( $>60$  min). In this regard, a simple colloidal silicic acid- $H_3PO_4$  employed by them would be the best emitter substance. The addition of GR to the colloidal silica which alone produced insufficient power intensity, however, improved the performance and would be expected to enhance the Pb ion beam intensity. But the GR addition to the 1 ng Pb sample gave ion beam intensity around  $0.5 \times 10^{-11}$  A of  $^{208}Pb$  that is lower than those expected from the results of 10, 5, and 2.5 ng Pb.

Therefore, it is needed to search the more suitable condition of GR to be able to apply to Pb isotope analysis of smaller samples. Moreover, referring the basic study by Kessinger *et al.* (2001) and Kessinger and Delmore (2002), further systematic investigation is required.

#### Measurements at UR

The measurements at UR were repeated several times for the samples: (A) 10 ng Pb, (B) 5 ng Pb and (C) 2.5 ng Pb, but were not duplicated for the samples that used only colloidal silica but no GR. Table 2 shows the Pb isotopic data, which were corrected for mass discrimination using a  $^{207}Pb$ - $^{204}Pb$  double-spiked run.

As shown in Table 2, the decay rates of the ion beams were 10% for the 10 ng Pb sample and 10–20% for the 5 ng Pb sample. The 2.5 ng Pb sample produced a series of high decay rates that ranged from 13.6–35.1%. The results presented here confirmed that the measurable duration of the ion beam was one hour or longer for the 10 and 5 ng Pb samples, and at least 30 min for the 2.5 ng Pb sample. 10 ng Pb and 5 ng Pb samples showed good performances in terms of intensity, stability, and duration of the ion beam relative to the performances of the samples (100, 50 and 10 ng) that did not include a GR addition.

The internal errors associated with the 2.5 ng Pb sample were larger by a factor of 2 than those of the 10 or 5 ng Pb samples. This observation was attributed to the small signals of 2.5 ng Pb sample, but the average values were consistent with the other samples within the error limits (Fig. 3).

The Pb isotope ratios for the GR-added samples were consistent with those observed in the samples that did not include a GR addition (UR). Thus, we calculated the following mean values from the data gathered in the present study:  $^{206}Pb/^{204}Pb = 16.9414 \pm 0.0036$ ,  $^{207}Pb/^{204}Pb = 15.4979 \pm 0.0048$ ,  $^{208}Pb/^{204}Pb = 36.7197 \pm 0.0121$  (errors are reported as twice the SD,  $n = 17$ ). The present results are compared well to those reported in previous studies using the double-spike or triple-spike correction, as shown in Table 2.

#### CONCLUDING REMARKS

1. To ensure reliable Pb isotope measurements from small samples, we developed a supplemental activator comprising 250 ng Ge and 500 ng Re (GR). The efficiency of the GR in conjunction with normal colloidal silica was confirmed in terms of enhancing and stabilizing the Pb ion beam for analysis measurements in which the sample contained as much as 2.5 ng Pb.

2. The new sensitive technique for precise Pb isotopic analysis is important for high-resolution studies, such as pollution history recorded in low Pb abundance coral skeletons.

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