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## Measurements of lithium isotopic compositions in coal using MC-ICP-MS

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Lithium is a very important metal for energy production. Lithium isotopes can be used to trace the source of fossil fuels that contribute to atmospheric haze and examine the occurrence and concentration of lithium in coal deposits. In this study, a microwave digestion method for coal decomposition using  $\text{HNO}_3 + \text{HF}$  and  $\text{H}_3\text{BO}_3$  acid systems was evaluated. The results demonstrated that coal was completely decomposed when these acids were used and the microwave program run in two steps. Three coal reference materials with different lithium concentrations (SARM18, SARM19 and SARM20) and four samples of Li-bearing coal from the Guanbanwusu Mine (China) were analyzed and the lithium isotopic composition was determined using MC-ICP-MS. Li isotope data were obtained with an intermediate precision better than  $\pm 0.30\text{‰}$ . The  $\delta^7\text{Li}$  values determined for SARM18, SARM19 and SARM20 were  $1.35 \pm 0.23\text{‰}$ ,  $2.16 \pm 0.27\text{‰}$  and  $1.48 \pm 0.17\text{‰}$ , respectively. The non-certified coal samples revealed a similar range in lithium isotopes ( $\delta^7\text{Li} = 6.02\text{‰}$  to  $6.77\text{‰}$ ) suggesting limited lithium isotope fractionation in coal locally, which could be useful for tracing atmospheric haze and contaminated waters in the environment. The comprehensive data and procedures in this study can be considered as a reference for conducting Li isotope determination in coal.

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### 1. Introduction

Trace elements in coal have attracted substantial research interest because of the increasing public concerns over the environmental pollution caused by coal production and utilization processes.<sup>1–4</sup> In China, some coal-associated lithium deposits have been found<sup>5–7</sup> and suggested to be a promising Li source, especially in countries with limited Li-bearing brines and pegmatites, because of the distribution and abundant global reserves of coal.<sup>8,9</sup> Additionally, Li isotopes in coal can not only be used to trace the source of fossil fuels contributing to atmospheric haze but can also provide information about the occurrence and concentration of lithium in coal deposits.

Coal is a complex mixture of organic matter and mineral matter, both of which are associated with many trace elements.<sup>10,11</sup> Therefore, coal decomposition is a very

important step in chemical analysis, and can be a limiting factor for quantitative elemental determination. Many digestion methods can be used in routine analysis of coal samples, including classical heating on a hot-plate, microwave assisted digestion, dry ashing, and alkali fusions.<sup>12,13</sup> Among them, microwave-assisted digestion became popular because it enables efficient decomposition of various types of sample matrices. This method is also well suited for coal.<sup>14–31</sup> In this study, coal samples were decomposed by microwave-assisted digestion in closed flasks using  $\text{HNO}_3 + \text{HF}$  and  $\text{H}_3\text{BO}_3$  for the purpose of determining the Li isotopic composition in coal using MC-ICP-MS.

### 2. Experimental

All experiments were carried out at the Institute of Earth Environment, Chinese Academy of Sciences (IEECAS).

#### 2.1. Instrumentation

A microwave-digestion system (model: UltraCLAVE, Milestone, Italy) was used for decomposition of samples.

Two ICP-MS instruments were employed: a Neptune Plus MC-ICP-MS (ThermoFisher, USA) for Li isotope determination and a PE NexION 300D ICP-MS (PerkinElmer, USA) for trace element determination. An iCAP<sup>TM</sup> 7400 ICP-OES (Thermo Fisher Scientific, Bremen, Germany) was employed for determination of major elements (K, Na, Ca, and Mg).

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## 2.2. Reagents and reference materials

BVIII grade (for electronic production) HNO<sub>3</sub> and HCl were sub-boiled using a Savillex DST-1000 system at a temperature <60 °C. Ultrapure grade HF (48%) and H<sub>3</sub>BO<sub>3</sub> (Supelco, Sigma-Aldrich) were directly used without further distillation. A NIST L-SVEC lithium carbonate standard, a seawater reference material for trace metals (NASS-6), an andesite powdered reference material (AGV-2), three certified coal samples (SARM18, SARM19 and SARM20) and non-certified coal samples collected from Li-bearing coal seam #6 in the Guanbanwusu Mine (China) were used. All the solutions were prepared using deionized water which was purified by using a Millipore system.

## 2.3. Sample preparation and digestion

First, coal samples were powdered to particles size <0.075 mm in an agate mortar. Approximately 20–50 mg of each powdered sample were weighed into a 15 mL Teflon microwave digestion vessel. Next, 4 mL of HNO<sub>3</sub> and 1 mL of HF were added. Samples were digested using an UltraCLAVE microwave digestion system (Milestone, Italy).<sup>40</sup> Five mL of H<sub>3</sub>BO<sub>3</sub> (3.8%) were added to each sample after being cooled to room temperature in a water bath. After H<sub>3</sub>BO<sub>3</sub> addition, the sample digestion was continued by repeating the temperature and pressure program given in Table 1. After digestion, the sample solutions were evaporated to dryness at 180 °C. Then they were diluted with 2% v/v HNO<sub>3</sub> to 10 mL and stored in a refrigerator prior to elemental or Li isotope determination.

## 2.4. Chemical purification

Before sample analysis by MC-ICP-MS, the sample solutions were purified to remove most matrix elements which could influence the Li isotope determination. Na is often present in the purified solution due to Na and Li having similar chemical properties and similar partition coefficients between the cationic resin and the acid medium. Phan *et al.*<sup>32</sup> found that Na has an insignificant effect on the Li isotopic ratio if Na/Li is higher than 5 under hot plasma conditions.

Lithium separation was performed in Savillex® microcolumns (0.64 cm ID × 25 cm height, 30 mL reservoir) packed with 8 mL of Bio-Rad® AG 50W X-12 cationic resin.<sup>32–35</sup> The procedure is detailed in Table 2. Prior to use, the resin was cleaned by alternatively rinsing with 8 M HNO<sub>3</sub> and H<sub>2</sub>O at least three times before storage in Milli-Q ultrapure H<sub>2</sub>O. Before the start of every chemical separation procedure, the resin was gently washed with

Table 2 Separation procedure for Li using AG50W-X8 resin in the column

Separation steps	Eluents	Volume/mL
Conditioning	0.5 M HNO <sub>3</sub>	16 (2 × 8 mL)
Sample loading	0.5 M HNO <sub>3</sub>	2 (1 × 2 mL)
Matrix rinsing	0.5 M HNO <sub>3</sub>	20 (5 × 4 mL)
Pre-check Li elution	0.5 M HNO <sub>3</sub>	2 (1 × 2 mL)
Li elution	0.5 M HNO <sub>3</sub>	25 (5 × 5 mL)
Tailing check	0.5 M HNO <sub>3</sub>	2 (1 × 2 mL)
Column cleaning	6 M HNO <sub>3</sub>	16 (2 × 8 mL)
	Milli-Q H <sub>2</sub> O	8 (1 × 8 mL)
	0.5 M HNO <sub>3</sub>	24 (3 × 8 mL)

a syringe with Milli-Q H<sub>2</sub>O to remove air bubbles and reduce resin compaction. The resin was conditioned with 16 mL of 0.5 M HNO<sub>3</sub>. Sample solutions were then loaded on the resin in the microcolumn followed by elution with 0.5 M HNO<sub>3</sub>. Matrix elements were firstly eluted with 20 mL of 0.5 M HNO<sub>3</sub>; subsequently, 29 mL of eluent containing Li were collected. In the next step, 16 mL of 6 M HCl were passed through the column. The collected 29 mL solution was divided in three portions: the first 2 mL were for pre-checking Li presence, the intermediate 25 mL were for Li isotope determination, and the last 2 mL were for checking Li tailing. Lithium isotopic ratios were determined when Li in the intermediate 25 mL was above 99.3%, taking into consideration that 29 mL solution was collected.

## 2.5. Li isotopic composition determination using MC-ICP-MS

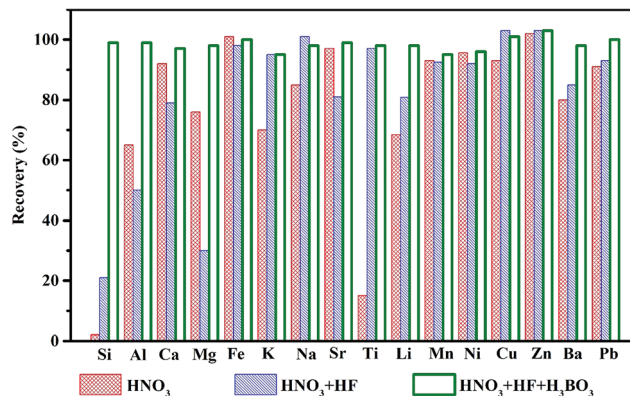
The collected 25 mL solution was evaporated to dryness, and residues dissolved in 2% v/v HNO<sub>3</sub> for Li isotope determination. For quality control purposes, each batch of samples was processed simultaneously with one blank and at least one reference material (*e.g.*, L-SVEC, NASS-6 or AGV-2). Sample duplicates were also occasionally added into the batch sequence. Lithium isotopic ratios were determined using the standard-sample bracketing (SSB) protocol using a NEPTUNE Plus MC-ICP-MS with a “wet” plasma introduction system at IEECAS. The operating parameters are provided in Table 3. <sup>6</sup>Li and <sup>7</sup>Li were measured simultaneously in separate Faraday cups (L4 and H4).<sup>36–39</sup> The background Li signal for <sup>7</sup>Li was <10<sup>-4</sup> V, which was negligible relative to the sample signals. The Li isotopic results are reported in δ notation in per mil relative to L-SVEC:  $\delta^7\text{Li} = [({}^7\text{Li}/{}^6\text{Li})_{\text{sample}}/({}^7\text{Li}/{}^6\text{Li})_{\text{L-SVEC}} - 1] \times 1000$ .

Table 1 Microwave program for sample digestion

Program/reagents	Stage	Time (min)	Temperature (°C)	Power (W)	Purpose
4 mL HNO <sub>3</sub> and 1 mL HF	1	15	0–210	2000	Warming up
	2	30	210	2000	Holding
	3	30	210–0	0	Cooling
4 mL HNO <sub>3</sub> , 1 mL HF and 5 mL H <sub>3</sub> BO <sub>3</sub>	1	15	0–210	2000	Warming up
	2	30	210	2000	Holding
	3	30	210–0	0	Cooling

**Table 3** Typical operating parameters for Li isotope measurement using a Neptune MC-ICP-MS

Parameters	Values
RF forward power (W)	1200
Ar cooling gas (L min <sup>-1</sup> )	15
Ar auxiliary gas (L min <sup>-1</sup> )	0.76
Ar sample gas (L min <sup>-1</sup> )	1.081
Extraction voltage (V)	-2000
Acceleration voltage (kV)	10
Detection system	L4 and H4 Faraday cups
Nebulizer	Low-flow PFA microcentric (50 μL min <sup>-1</sup> )
Focus Quad (V)	0.5
Dispersion (V)	26.5
Uptake time (s)	60
Integration time (s)	4.195
Measurement time (min)	4
Rinse time (min)	4

**Fig. 1** Elemental concentrations in certified coal (SARM19) acid digested using microwave radiation under the conditions given in Table 1. Major elements K, Ca, Na, and Mg were determined by ICP-OES and the other trace elements by ICP-MS.

### 3. Results and discussion

#### 3.1. Sample digestion

It has been reported that HNO<sub>3</sub>, HNO<sub>3</sub> + H<sub>2</sub>O<sub>2</sub> and HNO<sub>3</sub> + HF are commonly used to digest coal.<sup>15–30</sup> However, some solid residues remained after digestion using these reagent combinations as observed in previous studies.<sup>23,28</sup> The most abundant elements found in the residues were Si, Al and Ti when only HNO<sub>3</sub> was used, likely because HNO<sub>3</sub> was unable to completely decompose aluminosilicates and titanium salts present in the coal samples. When HF was added to the coal samples, the most abundant elements found were Ca, Mg and F. This was likely because HF reacted and generated insoluble fluorides, such as AlF<sub>3</sub>, CaF<sub>2</sub> and MgF<sub>2</sub>.

The use of H<sub>3</sub>BO<sub>3</sub> to solubilize the fluorides has been proposed in previous studies on trace element determination in coal fly ash and coal samples.<sup>18–20,23,28</sup> In the present study, HNO<sub>3</sub> alone, HNO<sub>3</sub> + HF and HNO<sub>3</sub> + HF + H<sub>3</sub>BO<sub>3</sub> were used to assess coal decomposition by means of a coal reference material (SARM19) analysis. Some residues were found after digestion using HNO<sub>3</sub> or HNO<sub>3</sub> + HF. However, no residues were found when using HNO<sub>3</sub> + HF + H<sub>3</sub>BO<sub>3</sub> due to solubilization of AlF<sub>3</sub>, CaF<sub>2</sub> and MgF<sub>2</sub> by H<sub>3</sub>BO<sub>3</sub>.

The recovery of each element was calculated and compared with the certified concentration value in the CRM (SARM19) as illustrated in Fig. 1. The results demonstrated that coal sample digestion by HNO<sub>3</sub> + HF + H<sub>3</sub>BO<sub>3</sub> was appropriate to determine the elemental concentration in coal, and the results agreed with the certified values.

Table 4 shows the Li concentration determined by ICP-MS. The Li concentrations in the three certified coal samples were in good agreement with the certified or reference values.

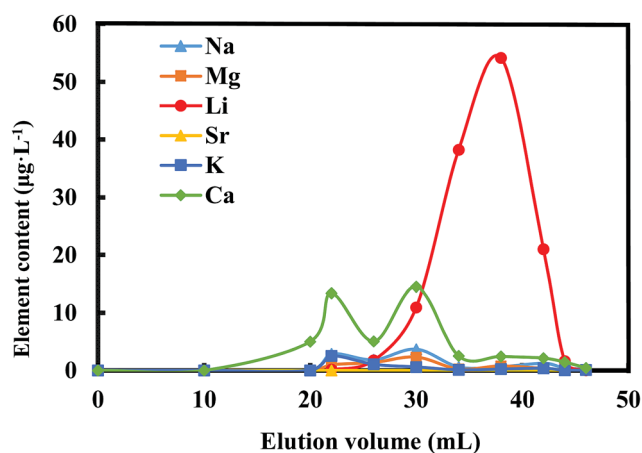
#### 3.2. Elution curves of Li in coal

Elution curves can vary based on the sample matrix. The elution curve for Li in coal must be determined to differentiate coal from other types of samples. SARM19 was used to test the efficiency of separating Li from other elements in the sample. The

**Table 4** Lithium concentration in three certified coals determined using ICP-MS after digestion with HNO<sub>3</sub> + HF + H<sub>3</sub>BO<sub>3</sub> (n = 4) assisted by microwave radiation

	Certified (μg g <sup>-1</sup> )	Found (μg g <sup>-1</sup> )	RSD (%)
SARM18	11.00	11.29 ± 0.18	0.51%
SARM19	37.00	36.92 ± 0.21	0.97%
SARM20	90.00	90.49 ± 0.28	1.32%

elution procedure detailed in section 2.4 was followed. Eluents were collected continuously every 1 mL. Then, 10 g L<sup>-1</sup> <sup>103</sup>Rb was added to all of the solutions as an internal reference for elemental analysis using ICP-MS. The elution curves are plotted in Fig. 2. The elution curve for coal was basically similar to those observed for lake water, river water and soil samples obtained in a previous study.<sup>39</sup> The elution position of Na, Mg, K and Sr remained basically unchanged. A small amount of Ca appeared in the elution curve of Li. Lithium did not appear in the eluent when the eluent volume was in the range of 0–20 mL. The

**Fig. 2** Elution curves of Li in coal.

concentration of Li in the eluent peaked when the eluent volume was about 38 mL and the volume for full Li recovery was 20–46 mL. To ensure a higher recovery of Li, the eluent collection must be 20–49 mL. Sodium was not detected in the eluent containing Li due to its prior separation in the column.

The Li recoveries for the processed SARM18, SARM19 and SARM20 solutions were 99.84%, 99.87% and 99.93%, respectively.

### 3.3. Precision and accuracy of Li isotope measurement

The precision and accuracy of the Li isotope determinations were derived by analyzing two in-house standards (IEECAS-Li

and SPEX-Li) and another in-house standard from the Isotopic Geochemical Laboratory of the University of Science and Technology of China (USTC, namely USTC-L) over a one-year period. A rock reference material (AGV-2) digested in the same way as coal and a seawater reference material (NASS-6) were purified following the same procedure and measured as well.

The measured  $\delta^7\text{Li}$  values for the three in-house standards were  $8.3 \pm 0.2\text{‰}$  ( $n = 43$ ),  $12.2 \pm 0.2\text{‰}$  ( $n = 59$ ) and  $19.3 \pm 0.1\text{‰}$  ( $n = 38$ ), which are in good agreement with published results.<sup>41</sup> The  $\delta^7\text{Li}$  values for the rock reference material (AGV-2) and seawater reference material (NASS-6) were  $30.81 \pm 0.38\text{‰}$  and  $6.01 \pm 0.10\text{‰}$ , respectively, and were in excellent agreement with previous studies as well (Table 5). A comparison of available Li isotope data with the results found in the present study indicates that precise and accurate Li isotopic data can be routinely obtained for rock and seawater.

### 3.4. Li isotopic composition in coal

Seven replicates of each reference material were digested and processed. The  $\delta^7\text{Li}$  values for the analyzed coal reference materials SARM18, SARM19, and SARM20 are shown in Fig. 3 and Table 6, being  $1.35 \pm 0.23\text{‰}$ ,  $2.16 \pm 0.27\text{‰}$  and  $1.48 \pm 0.17\text{‰}$ , respectively. These  $\delta^7\text{Li}$  values are within analytical uncertainty and lower than  $0.30\text{‰}$ . All samples were run at the same Li concentration and processed in the same way, but some

Table 5  $\delta^7\text{Li}$  in certified seawater and rock

Samples	$\delta^7\text{Li}$ (mean $\pm$ 2 SD‰)		
	This study ( $n = 5$ )	Reported	Ref.
Seawater (Atlantic NASS-6)	$30.81 \pm 0.38$	$30.87 \pm 0.15$	36
		$30.73 \pm 0.15$	34
		$30.64 \pm 0.44$	42
		$31.14 \pm 0.2$	43
		$30.55 \pm 0.45$	44
AGV-2	$6.01 \pm 0.10$	$5.68 \pm 1.04$	45
		$6.1 \pm 0.4$	46
		$6.85 \pm 0.20$	36

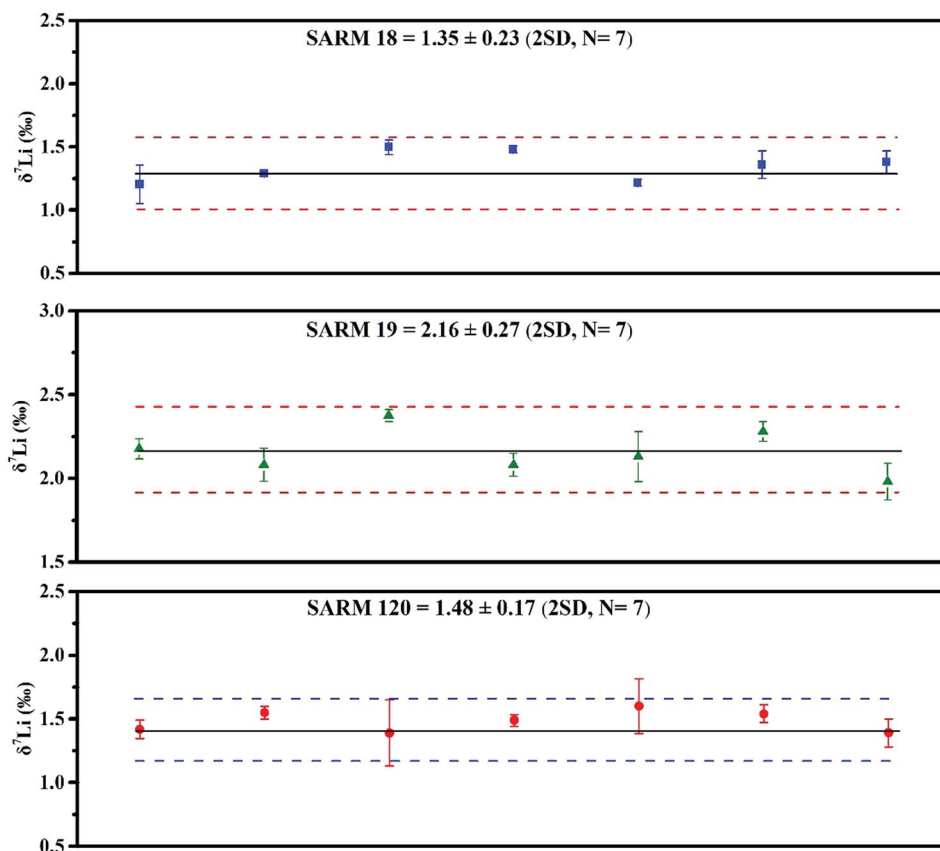


Fig. 3 Li isotopic composition in three coal reference materials. The  $\delta^7\text{Li}$  values are determined for 7 replicates of each sample ( $N = 7$ ).

Table 6  $\delta^7\text{Li}$  values found for certified coal

	$\delta^7\text{Li}$ (mean $\pm$ 2 SD‰, $n = 3$ )	$\delta^7\text{Li}$ (mean $\pm$ 2 SD‰, $n = 6$ )
SARM18	1.20 $\pm$ 0.15	1.35 $\pm$ 0.23
	1.38 $\pm$ 0.09	
	1.29 $\pm$ 0.02	
	1.49 $\pm$ 0.06	
	1.48 $\pm$ 0.03	
	1.22 $\pm$ 0.03	
SARM19	1.36 $\pm$ 0.11	2.16 $\pm$ 0.27
	2.18 $\pm$ 0.07	
	2.08 $\pm$ 0.10	
	2.37 $\pm$ 0.04	
	2.08 $\pm$ 0.07	
	2.13 $\pm$ 0.15	
SARM20	2.28 $\pm$ 0.06	1.48 $\pm$ 0.17
	1.98 $\pm$ 0.11	
	1.42 $\pm$ 0.07	
	1.55 $\pm$ 0.05	
	1.39 $\pm$ 0.26	
	1.49 $\pm$ 0.05	
	1.60 $\pm$ 0.21	
	1.54 $\pm$ 0.07	
	1.39 $\pm$ 0.11	

Table 7  $\delta^7\text{Li}$  values found for non-certified coal

No.	$\delta^7\text{Li}$ (mean $\pm$ 2 SD‰, $n = 3$ )
G9	6.03 $\pm$ 0.19
G10	6.51 $\pm$ 0.26
G11	6.59 $\pm$ 0.21
G14	6.77 $\pm$ 0.30
G45	7.86 $\pm$ 0.23

error bars in Fig. 3 are 2 times larger than the others indicating that other processes have an influence on the precision.

The  $\delta^7\text{Li}$  values for the non-certified coal ranged from 6.03‰ to 6.77‰, with an average of  $6.75 \pm 0.67\%$  (Table 7). These samples show a similar distribution in lithium isotopes, although they were collected in different layers of the coal mine, suggesting limited lithium isotope fractionation in coal at the same place. Coal from different regions may have different  $\delta^7\text{Li}$  values because the formation time and source were different. In addition,  $\delta^7\text{Li}$  in atmospheric haze can also be different. Therefore,  $\delta^7\text{Li}$  could be useful for tracing the source of fossil fuels or contaminated waters in the environment.

## 4. Conclusions

Coal submitted to microwave assisted digestion is efficiently decomposed using  $\text{HNO}_3 + \text{HF} + \text{H}_3\text{BO}_3$  and a temperature/pressure program run in two steps. Boric acid added in the second step solubilizes the fluorides formed from HF in the first step. High accuracy and precision of  $\delta^7\text{Li}$  measurement in coal were obtained using MC-ICP-MS. The  $\delta^7\text{Li}$  values of coal reference materials SARM18, SARM19, and SARM20 are  $1.35 \pm 0.23\%$ ,  $2.16 \pm 0.27\%$  and  $1.48 \pm 0.17\%$ , respectively. The

natural coal samples have limited lithium isotope fractionation ( $\delta^7\text{Li} = 6.02\%$  to  $6.77\%$ ) in different layers of the coal mine suggesting that  $\delta^7\text{Li}$  could be useful for tracing the source of fossil fuels or contaminated waters in the environment.

## Conflicts of interest

There are no conflicts to declare.

## Acknowledgements

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