Table A, Internet repository

Table A (Internet repository) Major and trace element composition of proximal and distal ash and tephra of 0.64 Ma Lava Creek tuff eruption of Yellowstone

Sample				SiO2	Al2O3	CaO	MgO	Na2O	K2O	Fe2O3	MnO	TiO2	P2O5	Cr2O3	LOI	Sum	Rb	Sr	Y	Zr	Nb	Ba
Lava Creek tuff B whole rock analyses																						
Proximal samples																						
LCT-2	Route 20 roadcut, Idaho	44°16'00"	111°28'05"	73.8	12.2	0.42	0.06	3.39	5.44	1.93	0.04	0.16	0.02		2.55	99.99	182	18	43	365	62	386
LCT-3a	Tuff Cliffs, Yellowstone caldera	44°39'05"	110°50'24"	78.1	11.2	0.35	0.03	3.25	4.34	1.39	0.02	0.1	0.01		1.1	99.89	199	10	68	185	49	129
IB01-1	Glenview, IA, Earthlodge			73.42	12.1	1.1	0.59	2.34	3.97	2.37	0.04	0.25	0.04	0.06	3.77	100.2	168	196	47	261	34	605
IB01-2	Spring Town quarry, NE	41°04'50.6"	96°04'26.2"	72.87	13.22	0.66	0.17	2.44	4.61	1.63	0.05	0.14	0.01	0.03	4.39	100.3	198	28	76	262	61	264
IB01-3	Frye et al 1948 J Geol photo, IA	41°51'23"	95°59'41.7"	70.1	14.6	0.72	0.19	2.41	4.19	2.07	0.26	0.17	0.03	0.04	4.54	99.47	169	47	68	304	66	639
JF01-2	IA ash, close to Frye et al			73.4	12.16	0.74	0.11	2.31	5.57	1.79	0.05	0.14	0.01	0.03	3.93	100.3	206	25	75	279	52	288
IB01-6	Richland ash, drillcore, SD	42°46'57.8"	96°40'49.5"	73.2	12.05	1.13	0.52	2.11	4.23	2.57	0.05	0.22	0.03	0.03	4	100.3	181	90	66	281	46	316
IB01-5-1	Hartford ash, drillcore, SD	43°39'14.3"	96°55'05.3"	73.48	12.67	0.67	0.21	2.68	4.71	1.7	0.06	0.15	0.01	0.03	3.85	100.3	213	27	74	306	61	185
Loess, overlying LCT																						
IB-01-5-7	Hartford ash, drillcore, SD, loess	43°39'14.3"	96°55'05.3"	72.74	12.87	1.17	1.18	1.27	2.44	3.00	0.06	0.51	0.07	0.02	4.62	100.1	143	194	52	370	34	609
Tephrochronological standards																						
LCT-B-standard				76.68	12.38	0.532	0.021	3.53	5.11	1.563	0.033	0.111				99.96						
				0.42	0.032	0.015	0.001	0.15	0.18	0.049	0.002	0.013										
Bishop Tuff -standard				77.38	12.736	0.4435	0.035	3.74	4.84	0.73	0.034	0.062				100.00						
				0.396	0.255	0.03	0.01	0.21	0.2	0.027	0.01	0.01										

Appendix (Internet Repository) Sulfate extraction and analysis techniques

Sulfate extraction procedures. Samples weighing between 30 and 100 g (most commonly 30-40g) were disaggregated and placed at the bottom of the glass beakers with 5vol% HCl in doubly deionized water so the sample/acid ratio was close to 1:10. The leaching solution was held at room temperature for 24 hours, and was stirred occasionally. Then, beakers were put in the hot cabinet held at 60°C for 2 hours and filtered through quantitative filter paper after that. This procedure leached all easily soluble compounds such as gypsum and carbonates, and the repeated leaching yielded no sulfate. In a few samples, carbonate cement dominated, and the solution bubbling occurred during the initial stages of acid addition. In these cases we waited for boiling to stop and added 10vol% HCl solution so the final solution was approximately at 5vol% HCl. Filtered solutions of ~250ml were placed in the same hot cabinet for evaporation, and $BaCl_2$ solution was added to them after the solutions were heated to slowly nucleate $BaSO_4$, and then left evaporating in the hot cabinet at 85°C for 24 hours until 30-50% of the initial volume of the solution remained. After 24 hours, variable amounts of white powder of $BaSO_4$ were formed at the bottom of the beaker. An excess of $BaCl_2$ was added to the solution again and left in a hot cabinet for another 2-3 hours, followed by the removal of the beaker from the hot cabinet and letting it cool for another 2 hours. The white powder at the bottom of the beaker was quite dense and no additional precipitation occurred in solution after adding more $BaCl_2$. $BaSO_4$ was then washed several times with dionized and then distilled water three times and then dried at 110°C. The sugar-white barite powder was collected from the bottom of each beaker and weighted. The proportion of SO_4 per one gram of sample was calculated (Table 1). Typically the described procedure generated between 4 and 100 mg of $BaSO_4$ for studied samples. Optical examination recorded that typical $BaSO_4$ sizes were 0.5-3 μm. XRD was performed on two powders, and confirmed that the white powder represented pure $BaSO_4$.

The 24h+2h at 85°C leaching procedure was repeated with 0.5 g of ash samples at 1:10 dilution, and the solutions were analyzed by the quadrupole ICP-MS methods for concentrations of cations and anions, including concentration of sulfur and selenium at the Department of Environmental Analysis Center at Caltech following standard procedures (N.D. Dalleska, director). The concentration of sulfur determined this way correlated with those determined by the direct weighing the barite powder .

Analysis. Samples of barite weighing 4-8mg were loaded in the Ni-plug and reacted with BrF_5 using the CO_2 laser beam to release oxygen. Only short, one, three, and five minutes BrF_5 pretreatment were performed after sample chamber evacuation. This cleaned the sample chamber of any traces of residual water. Typically 4 to 8 unknown barite samples were run during each analytical session together with silicate and barite standards. Loading more samples is not recommended as the BaF_2 window gets clouded from below after about 7 samples are run. The Gore Mountain Garnet standard ($\delta^{18}O$ =5.75‰) was run in the beginning of each day to ensure that the laser extraction line is yielding consistent results. During laser heating, most reaction occurs at low power, followed by boiling of the residue while increasing power to 10W that seems to generate no oxygen. Similar to observation of Bao et al. (2000), yellow liquid appears in the beginning of lasing but disappears after. The gentle laser power output increase in preferred to prevent sputtering and clouding the window.

The extracted oxygen passed through a series of cryogenic traps and hot mercury pump before been frozen into 3-5Å molecular sieve. The generated yield was determined using gas pressure in calibrated volume prior to freezing. This was done by the following procedure: weighted quantities of NBS127 and Aldrich barite standards were run and the generated oxygen was converted to CO_2 gas using carbon-rod converter. The amount of CO_2 corresponds to the O_2 but CO_2 gas is possible to freeze by liquid nitrogen in calibrated volume to determine quantity of gas in micromoles. The yields determined this way on barite standards were in 27-32% range, similar to yields obtained by Bao et al. (2000). The yields on the unknown barite samples were determined without conversion to CO_2 by registering the maximum pressure before freezing oxygen on a molecular sieve.

Such non-quantitative conversion implies that SOF_2 and/or SO_2F_2 compounds form as byproducts of the reaction, as was determined by the mass scan on the mass spectrometer. The non-quantitative but consistent yields require correction to the isotopic measurements of O_2 based on the value of standards. We used three Barite standards of known isotopic composition to monitor yield-$\delta^{18}O_{O2}$ relationship, and reproducibility: Baker Chemical, Aldrich, and NBS127. These samples were analyzed both as O_2 and CO_2 gas. The $\delta^{18}O_{O2}$ value of NBS127 barite standard ($\delta^{18}O_{O2}$ =9.3‰, Gonfiantini et al. 1995) in the laser chamber is +0.1±0.2‰, n=10, implying that there is a consistent 9.2‰ offset between the accepted value

and non-quantitatively extracted O_2 in the laser chamber. The NBS127 standard run twice as O_2 gas yielded $\Delta^{17}O=0.14\pm0.12‰$, and $0.21\pm0.11‰$. For Baker-4 standard, the $\delta^{18}O_{O2}$ value measured by the thermal combustion technique is $13.2\pm0.3‰$, n=4, P. Shanks, personal communication, 2004). The O_2 gas extracted from this standard by laser fluorination and run as O_2 gas on Finnigan 253 yielded $2.8\pm0.5‰$ (n=3), $\Delta^{17}O = -0.05\pm0.03‰$. Thus, the offset in $\delta^{18}O$ is 10.4‰. For the third, Aldrich barite standard ($\delta^{18}O =8.17‰$) the $\delta^{18}O$ value was $–0.84\pm0.2‰$ (n=6) and and $\Delta^{17}O=0.01\pm0.07‰$ (n=1), thus the offset was 9.0‰. Therefore, we accepted average 9.4‰ offset of our $\delta^{18}O$ measurements, and this value is similar to the value used by Bao et al. (2000) in their measurements.

Zero enrichment measurements on Finnigan 253 mass spectrometer during five analytical sessions averaged $–0.01\pm0.02‰$ for $\Delta^{17}O$, but the uncertainty on individual zero enrichment measurements averaged $\pm0.06‰$. Other silicate and oxide standards and materials were run in the same sample plug with barite samples during several analytical sessions. They yielded $\Delta^{17}O$ values near zero: Gore Mountain Garnet ($\delta^{18}O=5.7‰$, $\Delta^{17}O=0.15\pm0.10$, n=3), San Carlos Olivine ($\delta^{18}O=4.9‰$, $\Delta^{17}O=0.05\pm0.10$, n=1), synthetic aluminum oxide ($\delta^{18}O =15.2‰$, $\Delta^{17}O=0.04\pm0.10‰$, n=2), synthetic SiO_2 ($\delta^{18}O =23.95‰$, $\Delta^{17}O=0.17\pm0.09‰$, n=1). Slight deviations in $\delta^{18}O$ and $\Delta^{17}O$ values are likely due to the low-$\delta^{18}O$, high-$\Delta^{17}O$ blank from adjacent barite samples, but it produces no effect on our interpretation, because the measured $\delta^{18}O$ and $\Delta^{17}O$ ranges in barite are 30‰, and 3.5‰ respectively (Table 1). However, we do not assign mass-independent significance to $\Delta^{17}O$ value <0.20‰.

Rare Sulfur isotopic measurements. Purified powders of $BaSO_4$ were converted to Ag_2S following published techniques (Thode et al. 1961; Forrest and Newman, 1977; Farquhar et al. 2000). Barium sulfate powders (~1-10 mg) were placed in boiling flasks with ~25 ml of purified 'Thode' solution (500 ml HI, 816 ml concentrated HCl, 245 ml ~50 % H_3PO_2; Thode *et al*. 1961). The mixture was gently boiled for ~3 hours. A stream of N_2 gas carried evolved H_2S through a condenser and a milli-Q water trap before a trapping solution containing cadmium acetate absorbed the H_2S. The resulting CdS was converted to Ag_2S by adding ~5-10 drops of an ~0.1M silver nitrate solution to the trapping solution. The Ag_2S was filtered, washed (~150 ml deionized distilled water, ~10 ml 1M NH_4OH, ~150 ml deionized distilled water), and oven dried overnight at ~90°C.

Sulfur isotope analyses largely followed published methods (Hulston and Thode, 1965; Gao and Thiemens, 1991; Farquhar et al. 2000; Johnston et al. 2005). Silver sulfide powders (~1-3 mg) were weighed into small Al foil pouches and loaded into externally-heated Ni bombs. The bombs were evacuated for ~1-2 hours, cooled with liquid N_2, and filled with purified F_2 in stoichometric excess of that required for complete reaction of Ag_2S. The bombs were then heated to 270°C and held at temperature overnight. The SF_6 produced during this process was frozen into a U- trap cooled by liquid N_2 (-196°C), and non-condensable gaseous fluorine compounds were pacivated over a column of KBr held at 100°C. The trap was then warmed in an ethanol slush (~ -120°C) to separate the SF_6 from condensable impurities. The expanded SF_6 was frozen into the injection loop of a gas chromatograph (GC) and then carried by a He gas flow (~10 ml/min) through a composite GC column (6' - 1/8" Mol Sieve 5A column followed by a 12' - 1/8" HayeSep Q column) held at 50 °C. After SF_6 passed through the GC, the composite column was heated to 150°C and backflushed with He for ~20 minutes to avoid co-elution of contaminating compounds and later SF_6 samples. Purified SF_6 was introduced to a ThermoFinnigan MAT 253 dual-inlet gas-source mass spectrometer where sulfur isotope abundances were measured by monitoring the $^{32}SF_5^+$, $^{33}SF_5^+$, $^{34}SF_5^+$, and $^{36}SF_5^+$ ion beams at m/z = 127, 128, 129, and 131, respectively. Uncertainties associated with the sulfur isotopic measurements (0.07 ‰ for $_{-}^{34}S$, 0.006 ‰ for $\Delta^{33}S$, and 0.2‰ for $\Delta^{36}S$) are taken as the standard deviation associated with long-term repeat analyses (n = 26) of three International Atomic Energy Association silver sulfide standards.

Nitrate contamination check. We dissolved precipitated barite in DTPA agent: diethylene-triamine-penta-acetic acid [$(HO_2CCH_2)_2NCH_2CH_2]_2NCH_2CO_2H$]. The DTPA solution used for barite dissolution consisted of 0.05 M DTPA (98%) in a 1M NaOH solution. The generated solutions were diluted 100 times and run on an ion chromatograph at the Department of Chemistry, University of Oregon with the assistance of Prof. Paul Engelking. For the majority of samples nitrate concentration did not exceed 2%, and there is no correlation of measured $\Delta^{17}O$ with NO_3 present; for example Pinatubo samples with the highest NO_3 concentration of 3.6% have $\Delta^{17}O$ near zero.