SIMULTANEOUS PB-ISOTOPE AND TRACE-ELEMENT CHARACTERIZATION OF GALENA BY QUADRUPOLE-BASED LA-ICP-MS

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Highlights

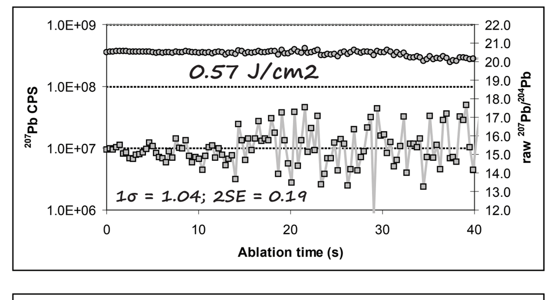
- Pb-isotopes measured by LA-quadrupole-ICP-MS in galena
- matrix-matched calibration using Broken Hill, NSW galena
- precision better than 0.1% achieved with 60 µm craters and n=20 spots per sample
- accuracy demonstrated relative to conventional TIMS data
- long-term reproducibility demonstrated
- extended range of elements enabled by fast-switched Q-filter: **Ag**, Cd, In, Sn, Sb, Te, **Tl**, Hg, **Pb**, Bi
- reconnaissance-level Pb isotopes in 20 minutes

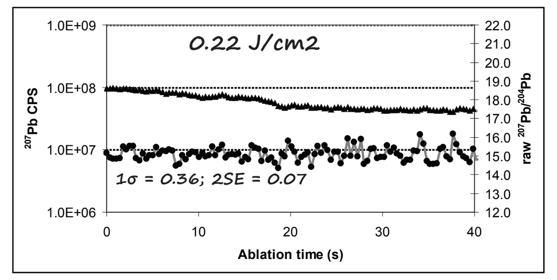
Optimization

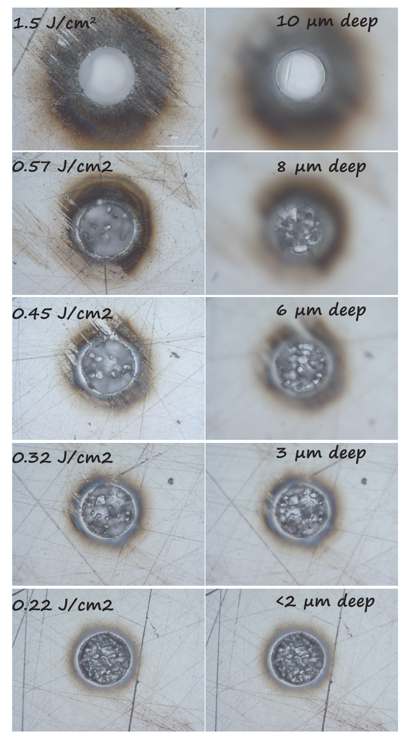
193nm laser (ASI M-50 with Laurin Tech S-155 cell)

The UNB laser ablation lab uses a 193 nm excimer laser (Coherent Compex Pro) with a nominal pulse width of 20 ns.

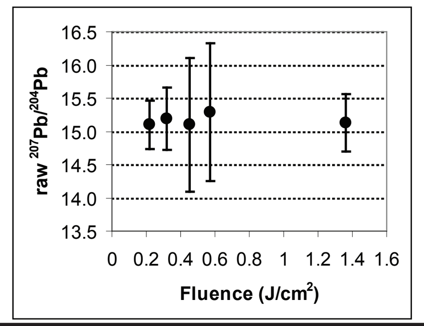
Galena is notoriously difficult to ablate in a controlled manner. Laser fluence was adjusted over a low energy range to identify conditions that yield lowest %RSD isotope ratio signals. Fluence of ~0.35 J/cm² provides a good compromise between stability of isotope ratios and efficient ablation of concentration standards (e.g., MASS1)



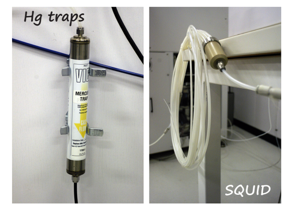




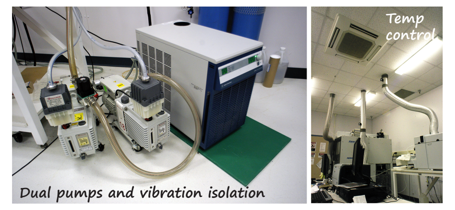
Galena is very sensitive to fluence. This optimization step is crucial to ensure low-noise ion beams to help minimize errors on Pb-isotope ratios. This approach should be used independent of the plasma-source platform (e.g., LA-MC-ICP-MS or LA-SF-ICP-MS)



Qadrupole ICP-MS (Agilent 7700x)



1. Hg traps on all gas lines (100 cps ^{204}Pb under max sensitivity)
2. Efficient signal smoothing
3. Dual rotary pumps
4. Minimal temperature fluctuations
5. Analyte dwell times, pulse rate (2.5Hz), and ablation time (45 s) optimized to achieve lowest %RSD
6. Torch and lens settings tuned to minimize mass bias on ^{207}Pb/^{206}Pb



Materials studied

1. Tynagh, Galway, Ireland
   Dixon, P.R., et al (1990; J. Geol. Soc 147, 121-132)
2. Telluride, Colorado
   Lipman et al. (1978; GSA Bulletin 89, 59-82)
3. Coeur D'Alene, Idaho
   Ramos, F.C. & Rosenberg, P. (2012; Econ. Geol. 107, 1321-1339)
4. Keno Hill, Yukon
   Goodwin, C.I. et al (1988; Leadtable: A Galena Lead Isotope Database for the Canadian Cordillera)
5. Bathurst, New Brunswick
   Thorpe, R.I. et al (1981; Trans. of the Inst. of Mining and Metallurgy, 1981, 90B, 55–56
6. Bilverinsgren (Iserholn), Germany
   Wedepohl, K.H. et al (1978; CMP 65, 273-281)
7. Walton and Jubilee, Nova Scotia
   Sangster, D.F. et al (1998; Econ. Geol 93, 911-919)
8. Mackenzie Gulch skarn, New Brunswick

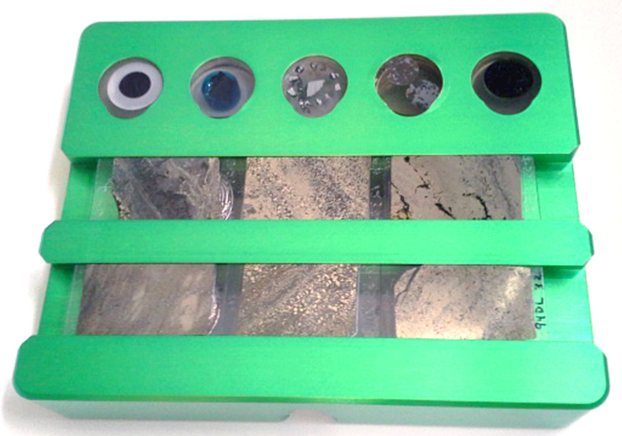
Matrix-matched calibration

A piece of galena from Broken Hill, NSW, was used as the primary reference standard with Pb isotope ratio values taken from Stacey, J. S. et al (1969; EPSL, 6(1), 15-25).

Concentrations of Ag, Cd, In, Sn, Sb, Te, Tl and Bi were measured by LA-ICP-MS in-house using USGS MASS-1 for calibration and an internal standard value of 86 wt% Pb. Accuracy of the data were checked by replicate analysis of USGS GSE1-G glass distributed throughout the ablation sequence.

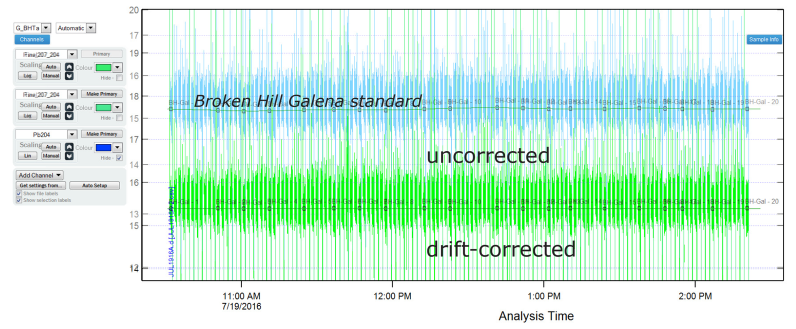
Standard Name G_BH
Data source Stacey et al, 1969 EPSL
Matrix Galena
Brief description "Broken Hill NSW, galena natural standard"
Notes
URL

Parameter	Units	Value	Uncertainty
Age	Ma	1600	5
Ag	ppm	340	50
Cd	ppm	50	20
In	ppm	0.202	0.02
Sn	ppm	63	2.1
Sb	ppm	390	50
Te	ppm	0.3	0.1
Hg	ppm	0.1	0.1
Tl	ppm	2.0	0.2
Pb	ppm	850000	10000
Bi	ppm	2.57	0.05
Th	ppm	0.01	0.01
U	ppm	0.01	0.01
207Pb/206Pb		0.9617	0.0005
208Pb/206Pb		2.2294	0.0005
206Pb/208Pb		0.4485	0.0002
206Pb/204Pb		16.007	0.007
207Pb/204Pb		15.397	0.007
208Pb/204Pb		35.675	0.010

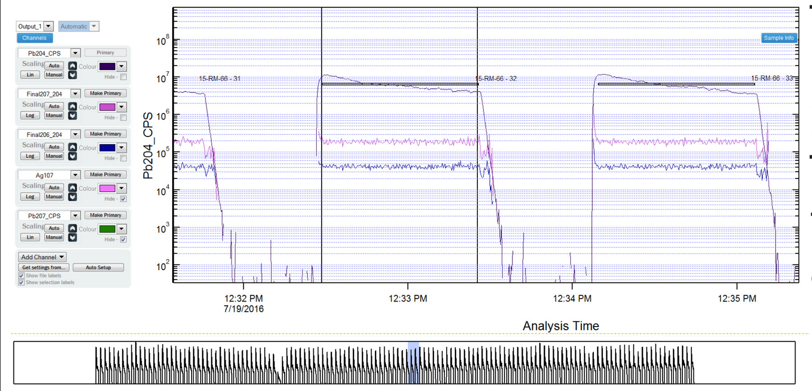


A typical session comprised at least 20 ablations for each sample, using single large grains or disseminated multi-grain populations. Laser and ICP-MS conditions were set to optimized conditions. At least 15 Broken Hill galena ablations were obtained and distributed throughout the run to correct for instrument drift and mass bias. Ablations were typically 40-60 seconds at 2.5 Hz with 40 seconds of background collection. No pre-ablation was used, but the data were cropped offline to exlude the first two seconds of signal rise time.

Data reduction



Data were reduced using a modified version of the VizualAge data reduction scheme (DRS) in Iolitev3.32. The DRS was modified to apply a drift correction (auto spline) to Pb isotope ratios based on the measured BH Galena standard. A mass bias correction was then applied based on the measured/true isotope ratios for BH Galena defined in the standard file.



Time-series for unknowns were inspected and trimmed if necessary of domains that encountered inclusions (rare). Iolite's 3σ outlier rejection was also used.
The final errors are fully propagated from internal errors for each integration and excess error from the standard analyses. Errors are reported at 2S.E.

No Pb carry-over was observed despite average total Pb ion beams upwards of 4E8 cps.

Future work

- Establish method for minerals with lower Pb concentrations
- fully calibrate fluence response
- Extend to other isotope systems such as Tl
- Assess intergranular Pb isotopic heterogeneity relative to chemical variations

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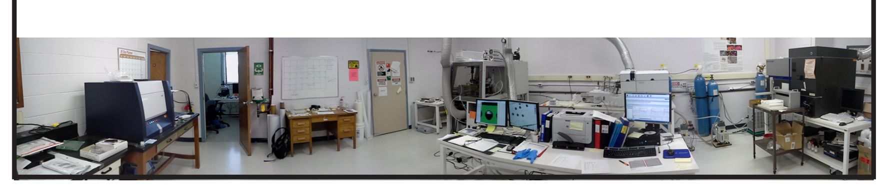
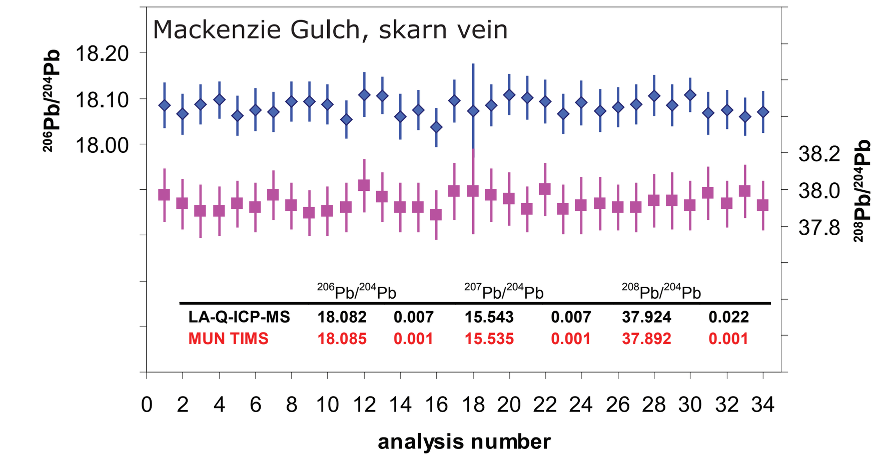
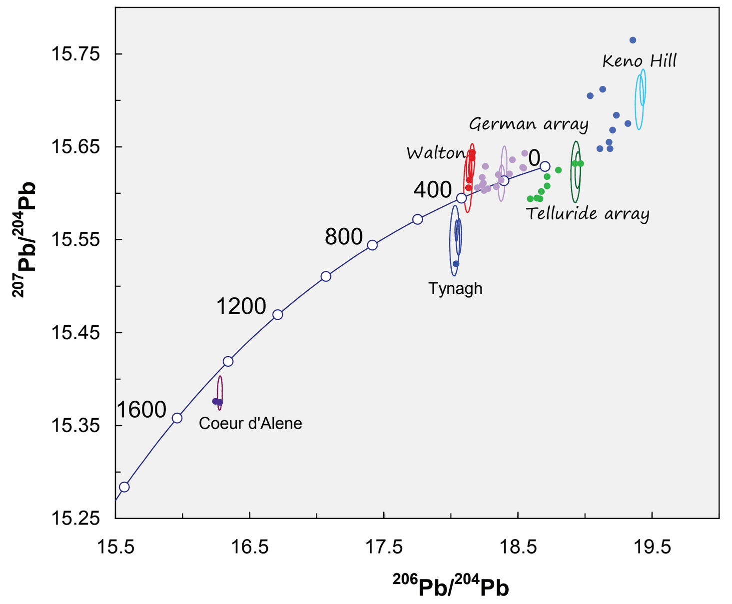


Accuracy & Precision

A galena-bearing thin section from the Mackenzie Gulch skarn deposit was analyzed in-house by LA-Q-ICP-MS and by conventional whole rock TIMS at Memorial University of Newfoundland (MUN). The data are in excellent agreement at the 2S.E. level



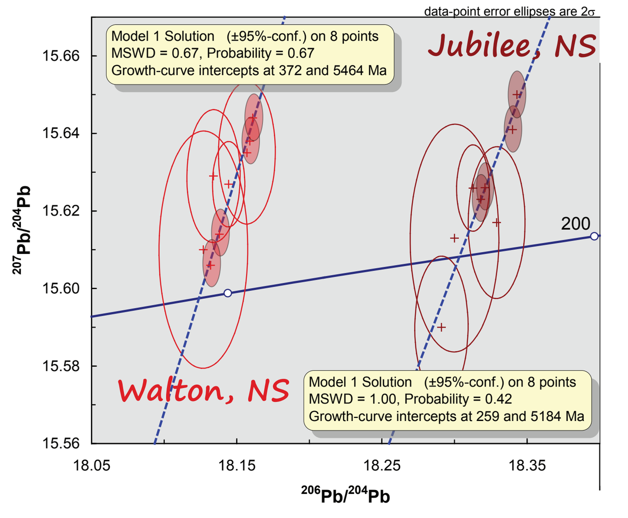
Weighted means (Isoplot v3.71) with errors of <0.1% are sufficient for regional-level tracer isotope studies. The methodology easily resolved differences among a variety of deposits



These tests indicate that the proposed methodology is both accurate and precise enough to conduct routine exploratory or reconnaissance Pb-Pb isoitope work on galena. Grain sizes of ~100 µm are suitable targets.

Reproducibility

Four analytical sessions between July and September 2016 yield demonstrably reproducible data.



Comments	Date	^{207}Pb/^{206}Pb	2S.E.	^{206}Pb/^{208}Pb	2S.E.	^{206}Pb/^{204}Pb	2S.E.	^{207}Pb/^{204}Pb	2S.E.	^{208}Pb/^{204}Pb	2S.E.
Jubilee, NS	7-Jul	0.8533	0.0082	0.4789	0.0007	18.300	0.025	15.613	0.024	38.21	0.06
LA-Q-ICP-MS	11-Jul	0.8528	0.0008	0.4806	0.0005	18.329	0.016	15.617	0.016	38.23	0.05
	19-Jul	0.8534	0.0004	0.4788	0.0003	18.313	0.009	15.626	0.009	38.24	0.03
	13-Sep	0.8542	0.0010	0.4775	0.0005	18.291	0.015	15.590	0.015	38.23	0.05
Reference values							2σ		2σ		2σ
Sangster et al 1998		0.8528		0.4788		18.340	0.005	15.641	0.005	38.30	0.02
"		0.8532		0.4785		18.343	0.005	15.650	0.005	38.33	0.02
"		0.8529		0.4789		18.321	0.005	15.626	0.005	38.25	0.02
"		0.8529		0.4794		18.318	0.005	15.623	0.005	38.21	0.02

Comments	Date	^{207}Pb/^{206}Pb	2S.E.	^{206}Pb/^{208}Pb	2S.E.	^{206}Pb/^{204}Pb	2S.E.	^{207}Pb/^{204}Pb	2S.E.	^{208}Pb/^{204}Pb	2S.E.
Walton, NS	7-Jul	0.8622	0.0008	0.4749	0.0007	18.127	0.025	15.610	0.025	38.13	0.06
LA-Q-ICP-MS	11-Jul	0.8611	0.0008	0.4764	0.0005	18.157	0.016	15.635	0.015	38.19	0.04
	19-Jul	0.8614	0.0004	0.4751	0.0003	18.144	0.009	15.627	0.009	38.19	0.03
	13-Sep	0.8609	0.0010	0.4752	0.0005	18.134	0.015	15.629	0.014	38.16	0.04
References values							2σ		2σ		2σ
Sangster et al 1998		0.8612		0.4747		18.159	0.005	15.638	0.005	38.26	0.02
"		0.8608		0.4751		18.138	0.005	15.614	0.005	38.18	0.02
"		0.8607		0.4754		18.132	0.005	15.606	0.005	38.14	0.02
"		0.8614		0.4739		18.161	0.005	15.644	0.005	38.33	0.02

Trace element variations

Simultaneous characterization of trace elements in galena can provide additional criteria to augment the Pb-Pb tracer isotope system.