Precise lead isotope ratios in Australian galena samples by high resolution inductively coupled plasma mass spectrometry

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High resolution inductively coupled plasma mass spectrometry (HR-ICP-MS) was used to measure Pb isotope ratios in standard solutions and Pb mineral digests. The RSD values obtained for $^{208}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$, $^{206}Pb/^{204}Pb$, $^{208}Pb/^{206}Pb$ and $^{207}Pb/^{206}Pb$ were 0.13, 0.11, 0.11, 0.046 and 0.048%, respectively (values as 1σ). These values were obtained from 30 analyses of three different standard sample types (multi-element standard, NIST SRM 981 and a Broken Hill galena digest). Based on 39 analyses of 11 galena samples from different locations around Australia, the difference between HR-ICP-MS and conventional TIMS values for $^{208}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$, $^{206}Pb/^{204}Pb$, $^{208}Pb/^{206}Pb$ and $^{207}Pb/^{206}Pb$ ratios was generally better than $\pm 0.2\%$. This paper outlines a very simple and rapid analytical method for the measurement of Pb isotope ratios, and is one of the first studies to use HR-ICP-MS to measure Pb isotope ratios in galena and galena-bearing ores.

Keywords: *Lead isotope ratios; high resolution inductively coupled plasma mass spectrometry; galena; ores*

The study of the isotopic composition of Pb in rocks and minerals began over 80 years ago and was initially used as a geochronological tool.[1] Subsequent work showed that for many types of geological materials, Pb isotope geochronology was complicated by the presence of 'common' Pb (*i.e.*, non-radiogenic Pb).[2] Hence today, Pb isotope geochronology uses minerals that formed with very little Pb.[3] However, a second important practical application of Pb isotopes is in studying and exploring for mineral deposits.[4] The Pb isotope composition of rocks and Pb-bearing minerals can be used to trace the sources of metal in ores and to help discriminate barren from mineralised ore systems.

At present, thermal ionisation mass spectrometry (TIMS) is the technique of choice for all types of geological Pb isotope measurements. However, the relatively high cost of TIMS instrumentation and the (necessary) extensive chemical pre-treatment of the sample prior to analysis have imposed serious limitations on the routine use of TIMS techniques in geochemical exploration applications.

Quadrupole based ICP-MS instruments have been used in many studies to measure Pb isotope ratios.[5–8] However, owing to the design and manner in which quadrupole mass analysers operate, the technique has been found to be limited in both precision and accuracy. The precision of isotope ratios measured on quadrupole ICP-MS instruments is typically 0.1% RSD, whereas for ratios involving a low abundance isotope such as ^{204}Pb, a precision of 0.2–1% RSD is usually obtained.[8]

Recently, Begley and Sharp[8] undertook an elegant study of Pb isotope ratios using a quadrupole ICP-MS instrument.

After careful consideration of all possible causes of instrumental bias, the precision obtained from the analysis of NIST Standard Reference Material (SRM) 981 Natural Lead ranged from 0.04 to 0.12%, depending on the ratio considered. The accuracy and precision reported may be the best obtained from a quadrupole instrument. However, the methodology and detail required to obtain such results could not be called routine.

High resolution ICP-MS (HR-ICP-MS) is a relatively new technique employing a magnetic sector mass analyser. To date it has been applied in a variety of areas such as environmental and biological analysis and the monitoring of radionuclides (see the review by Becker and Dietze[9]). Only a limited number of studies have been reported on measuring isotope ratios.[10–14] With regard to Pb isotope ratios, Vanhaecke *et al.*[10] obtained a precision of 0.04% ($n=10$) for the $^{206}Pb/^{207}Pb$ ratio in a standard lead solution. Little has been reported about the Pb isotope ratio analysis of geological matrices.[14] It should also be noted, however, that double focusing multiple collector ICP-MS instruments have been used recently to measure highly accurate isotope ratios (including Pb), and may see increased use in future work.[15,16]

In this paper, a fast and reliable method for the precise measurement of Pb isotope ratios in geological samples by HR-ICP-MS is reported. The technique was applied to the measurement of the Pb isotope composition of galena and galena-bearing ores from Broken Hill and Western Tasmania, previously measured by TIMS.

EXPERIMENTAL

Reagents

High purity HCl was prepared by doubly quartz distilling analytical-reagent grade acid (Merck, Darmstadt, Germany), and high purity HF was prepared from analytical-reagent grade acid (Merck) that had been further purified *via* a Teflon distillation system. High purity HNO_3 (Mallinckrodt, St. Louis, MO, USA) was used as received for sample digestion and solution acidification. Ultra-pure de-ionised water (≥ 18 MΩ) was prepared *via* a glass distillation unit followed by further purification with a Modulad water purification system (Continental Water System, Melbourne, Australia).

Standards and sample preparation

Instrument tuning and general Pb solutions were prepared by dilution from a Perkin-Elmer (Norwalk, CT, USA) 10 µg g^{-1} multi-element solution containing Pb (Cat. No. N930–0233).

A stock standard solution of NIST SRM 981 Natural Lead was prepared by dissolving 0.05 g of Pb in 5 ml of dilute HNO_3 ($1+4$) with heating in a Savillex screw-topped Teflon

beaker.[17] After cooling to room temperature, 1 ml of concentrated HNO_3 was added before dilution to 100 ml total volume (in polycarbonate). The stock standard solution was diluted to working concentrations (generally 10–50 ng g^{-1}) before analysis. This reference solution was used as the external calibration standard in this study.

Galena sample solutions were prepared as follows. Samples were dried at 105 °C overnight and 0.1 g portions were added to Savillex screw-topped Teflon beakers. A 5 ml volume of HF–HNO_3–HCl (2+1+3) acid mixture was added to each sample[18] with overnight heating on a hot-plate at 130 °C. The resulting solution was twice evaporated to incipient dryness, with the addition of 1 ml of HNO_3 after each drying stage. All solutions were stored in sealed polycarbonate containers. Galena solutions were diluted to a Pb concentration between 40 and 50 ng g^{-1} for HR-ICP-MS analysis.

Instrumentation

Pb isotope ratios were measured on an Element HR-ICP-MS instrument (Finnigan MAT, Bremen, Germany). This instrument, utilising a magnetic sector mass analyser of reversed Nier–Johnson geometry, has pre-defined resolution settings ($m/\Delta m$ at 10% valley definition) of 300 (low), 3000 (medium) and 7500 (high). A resolution of 300 was used in this work, providing flat-topped peaks and maximum instrument sensitivity (typically greater than 10^6 counts s^{-1} for 10 ng g^{-1} ^{115}In or 7×10^5 counts s^{-1} for 10 ng g^{-1} ^{208}Pb). Instrument and method settings are outlined in Tables 1 and 2. A standard Meinhard nebuliser and Scott double pass water cooled spray chamber were employed. Isotopes of interest were analysed using electric scanning with the magnet held at fixed mass. The secondary electron multiplier detector (with discrete dynodes) was operated in the counting mode. Instrument tuning and optimisation were performed daily using a 10 ng g^{-1} multi-element solution containing Pb. Further details concerning this instrument have been reported elsewhere.[19–21]

All isotope ratio values were adjusted for instrument dead time.[22] Each Pb isotope ratio was considered in dead time determinations. The dead time was measured regularly throughout the study using three Pb solutions of different concentrations, namely 10, 25 and 50 ng g^{-1} Pb. Dead time values in the range 20–50 ns were typically found, depending on the detector settings. Analyses were also blank corrected.

Table 1 Typical instrumental configuration and settings

Instrument	Finnigan MAT Element
Resolution ($m/\Delta m$)	300 (low)
Rf power	1250 W
Nebuliser	Meinhard concentric
Coolant argon flow rate	$\sim$12.5 l min^{-1}*
Auxiliary argon flow rate	$\sim$1.1 l min^{-1}*
Nebuliser argon flow rate	$\sim$1.1 l min^{-1}*
Spray chamber	Scott (double pass) type cooled to 3.5–5 °C
Sampler cone	Nickel, 1.1 mm aperture id
Skimmer cone	Nickel, 0.8 mm aperture id
Instrument tuning	Performed using a 10 ng g^{-1} multi-element solution
Ion transmission	Typically 10^6 counts s^{-1} per 10 ng g^{-1} ^{115}In or 7×10^5 counts s^{-1} for 10 ng g^{-1} ^{208}Pb
Scan type	Fixed magnet with electric scan over small mass range
Ion sampling depth	Adjusted daily*
Ion lens settings	Adjusted daily†

* Adjusted in order to obtain maximum signal intensity. † Adjusted in order to obtain maximum signal intensity and optimum resolution.

Table 2 Method parameters for Pb isotope ratio measurements

Isotopes considered	^{201}Hg or ^{202}Hg, ^{204}Pb, ^{206}Pb, ^{207}Pb and ^{208}Pb
Scan type	Magnet fixed at ^{201}Hg. Electric scans over other mass ranges
Mass scanning window	3%
Magnet settle time	0.1 s
Dwell time per measurement	0.001 s
Scan duration per sweep	5×0.025 s
Number of sweeps	2000
Measurement time per replicate	250 s
Detector mode	Counting
Integration type	Average
Sample uptake and equilibration time	2 min
Rinse time between each sample	3–5 min (with 5% HNO_3)
Total time per sample	$\sim$15 min
Measured dead time	In the range 20–50 ns, depending on detector settings

RESULTS AND DISCUSSION

Mass discrimination correction

Isotope ratio values obtained using ICP-MS may deviate from the 'true' value as a function of the difference in mass between the two isotopes measured. This effect is defined as mass bias and its value may be either positive or negative.[23] The bias or discrimination can only be determined experimentally and will vary with the configuration of the individual ICP-MS system.[22] In this study, instrument mass discrimination was corrected by the use of a NIST SRM 981 external standard. Unknown samples to be measured were typically analysed between alternate standard reference solutions. The use of this correction method allows any measured differences in a Pb standard sample to correct the ratios found in unknown Pb solutions (i.e., Pb standards correcting for Pb unknowns). Also, similar isotope abundances are typically measured for both standards and unknowns. However, on the negative side, there is a time delay between each standard and sample in which changes in plasma conditions can occur. The other option of using a Tl internal standard for mass discrimination correction was not investigated in this study. This method involves measuring another isotope (Tl) which may behave in a different fashion to Pb whilst also increasing the analysis time for each scan (time which could be spent accumulating Pb data). The internal correction approach has an advantage, however, of continuously monitoring the mass discrimination for each individual sample. Both methods have been used in previous Pb isotope studies[6–8,11] and were outlined in detail by Begley and Sharp.[8]

General analytical and methodology considerations

Method parameters were systematically varied and tested in order to obtain the most accurate and precise Pb isotope ratios. The first variable considered was the number of scans for each sample. The ideal situation would be to acquire as many scans as possible in the shortest time interval, hence approaching the behaviour of a multiple collector system. The number of sweeps across the Pb isotopes was varied between 500 (total analysis time 62.5 s) and 3000 (375 s), with 2000 scans (250 s) proving optimum considering Pb signal stabilities. All scanning protocols were at a rate of 8 sweeps s^{-1}, keeping the dwell time for each mass segment constant. Vanhaecke et al.[10] used 1200 scans in 2 min to measure ^{206}Pb/^{207}Pb isotope ratios in a standard Pb solution.

Vanhaecke et al.[11] also found that when considering both Pb or Cu isotope ratios at resolution 3000 using HR-ICP-MS,
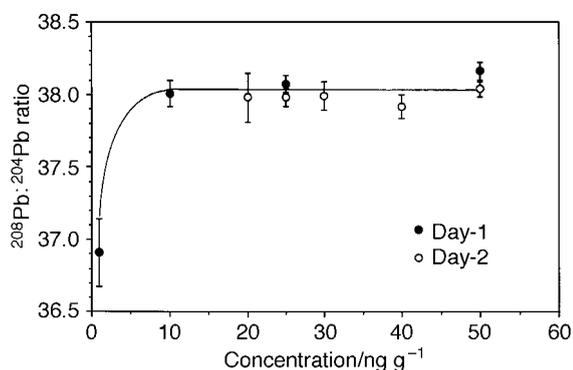
Fig. 1 Measured $^{208}Pb/^{204}Pb$ ratios *versus* Pb concentration in standard solutions. Ratios were measured over two consecutive days. Note that the values shown have not been corrected for any mass discrimination.

the precision was improved when the mass scanning window was reduced from 20 to 10% (the percentage window value is based on the expected mass width of a peak in the respective resolution). It was suggested that when smaller mass windows were used, only the centre of each peak was scanned, minimising the influence of any mass calibration instabilities. Although more crucial at resolution 3000 away from the flat-topped peaks of resolution 300, a similar systematic study was undertaken in this work, considering Pb ratios at low resolution. Mass windows between 1 and 10% were considered, and it was found that a mass scanning window of 3% gave isotope signals with minimum variation over the total number of scans.

The working Pb concentration range for which accurate Pb isotope ratios could be obtained was also investigated. At Pb concentrations below 10 ng g^{-1}, ratios with ^{204}Pb as the basis were found to be limited by counting statistics, resulting in less accurate results (a concentration of 10 ng g^{-1} corresponded to approximately 15 000 counts s^{-1} of ^{204}Pb). This is shown more clearly in Fig. 1 for the $^{208}Pb/^{204}Pb$ ratio measured in Pb standard solutions of various concentrations analysed over two consecutive days. Similar results were found for the other Pb ratios considered. This has not been noted as a problem in other HR-ICP-MS studies as the ratios investigated have typically involved ^{206}Pb, ^{207}Pb and ^{208}Pb isotopes only.[10,14] At the other extreme, Pb concentrations above 50 ng g^{-1} were not considered as the signal from ^{208}Pb required measurement in the analogue detector mode to avoid detector saturation (under normal operating conditions and detector settings, 50 ng g^{-1} of ^{208}Pb corresponded to 3×10^6–3.5×10^6 counts s^{-1}). Rather than limit the accuracy of the ratio determinations it was decided to make all measurements in the same detector mode (counting). Hence ratios were only determined in the Pb

concentration range 10–50 ng g^{-1}. Work is continuing to increase the concentration range for which accurate Pb ratios can be obtained.

All ratio measurements were dead time corrected. Even with this adjustment, it was found that the accuracy of each measurement could be further improved when the Pb concentration in the NIST SRM 981 external calibration standard and the unknown sample were closely matched. As such the concentration of Pb in each sample was often adjusted prior to ratio determinations.

Along with the four Pb isotopes of interest, ^{202}Hg and ^{201}Hg were also measured as ^{204}Pb (1.4% abundant) has an isobaric interference from ^{204}Hg (6.85% abundant) in resolution 300. For geological samples that were previously ground in tungsten crushing mills, ^{201}Hg was used to correct ^{204}Pb, as ^{202}Hg suffers interference by $^{186}W^{16}O$.[7] For other samples ^{202}Hg was used. It was expected that during sample digestion any volatile Hg would be driven off during the multiple drying stages, while the Hg : Pb ratio in rocks and sulfides is generally low (1 : 10–100).[24] No samples analysed in this study were found to have appreciable levels of Hg or W. However, it was important to include these isotopes in method development work for future samples when more appreciable Hg or W concentrations may be encountered.

Precision

Lead isotope ratio precision data for 10 consecutive measurements of three different standard solutions are given in Table 3. Precisions obtained for ratios involving the low abundance ^{204}Pb isotope were 0.10–0.13% for $^{208}Pb/^{204}Pb$, 0.10–0.11% for $^{207}Pb/^{204}Pb$ and 0.10–0.11% for $^{206}Pb/^{204}Pb$ (values as 1σ). Improved precisions were found for those ratios involving the more abundant isotopes, namely 0.041–0.046% for $^{208}Pb/^{206}Pb$ and 0.044–0.048% for $^{207}Pb/^{206}Pb$. No difference in measurement precision was apparent between standard Pb solutions and more 'complex' galena digest samples. Theoretical precisions based on Poisson counting statistics were also calculated and are shown in Table 3 (based on ^{208}Pb signals of the order of 1×10^6–3×10^6 counts s^{-1}). In agreement with other workers,[13] external precisions approximately 2–3 times greater than that predicted from counting statistics alone were found, suggesting noise contributions from other sources such as the sample introduction system and plasma flicker. The precisions obtained for ratios referenced to ^{206}Pb are similar to that found by Vanhaecke *et al.*[10] using a similar HR-ICP-MS instrument to measure the $^{206}Pb/^{207}Pb$ ratio of a standard Pb solution. The external precisions given in Table 3 are also similar to the best obtained using a quadrupole ICP-MS by Begley and Sharp.[8]

Table 3 Pb isotope ratio precision and accuracy data for a standard multi-element solution, NIST SRM 981 and a Broken Hill galena digest. Samples were analysed at a Pb concentration of 45 ng g^{-1}

	$^{208}Pb/^{204}Pb$	$^{207}Pb/^{204}Pb$	$^{206}Pb/^{204}Pb$	$^{208}Pb/^{206}Pb$	$^{207}Pb/^{206}Pb$
Multi-element standard solution—					
Precision for 10 measurements, RSD (%)	0.11	0.11	0.10	0.041	0.047
Theoretical RSD (%)*	0.054	0.055	0.055	0.015	0.016
NIST SRM 981 Natural Lead—					
Precision for 10 measurements, RSD (%)	0.10	0.11	0.11	0.046	0.048
Theoretical RSD (%)*	0.049	0.050	0.050	0.014	0.015
Broken Hill galena—					
Measured ratio	35.520	15.353	15.985	2.222	0.961
Reference value†	35.599	15.370	15.994	2.226	0.961
ICP-MS bias from TIMS value (%)	−0.22	−0.11	−0.06	−0.18	0
Precision for 10 measurements, RSD (%)	0.13	0.10	0.11	0.043	0.044
Theoretical RSD (%)*	0.052	0.053	0.053	0.015	0.016

* From Poisson counting statistics. † From TIMS analysis.

Table 4 Measured Pb isotope ratios in selected Australian galena samples. Ratios from HR-ICP-MS and TIMS are compared

Sample code	Deposit location	n*	208/204			207/204			206/204			208/206			207/206		
			ICP-MS	TIMS	Δ† (%)	ICP-MS	TIMS	Δ† (%)	ICP-MS	TIMS	Δ† (%)	ICP-MS	TIMS	Δ† (%)	ICP-MS	TIMS	Δ† (%)
Z5199	Oceana	2	38.222	38.121	+0.26	15.603	15.607	−0.03	18.315	18.281	+0.19	2.0868	2.0853	+0.07	0.8519	0.8537	−0.21
Z5221	Argent 2	3	38.402	38.417	−0.04	15.651	15.622	+0.19	18.492	18.531	−0.21	2.0753	2.0731	+0.11	0.8458	0.8430	+0.33
Z5232	Swansea	3	38.240	38.241	−0.003	15.648	15.633	+0.10	18.331	18.368	−0.20	2.0894	2.0819	+0.36	0.8550	0.8511	+0.46
Z5237	Montana	3	38.474	38.472	+0.005	15.644	15.625	+0.12	18.550	18.561	−0.06	2.0753	2.0727	+0.13	0.8439	0.8418	+0.24
Z5277	N. Tas. Mine	3	38.288	38.296	−0.02	15.620	15.624	−0.03	18.423	18.428	−0.03	2.0841	2.0781	+0.29	0.8502	0.8478	+0.28
H15	Hellyer	2	38.241	38.178	+0.17	15.634	15.612	+0.14	18.380	18.361	+0.10	2.0781	2.0793	−0.06	0.8502	0.8503	−0.01
EB1007	Elliot Bay	2	37.868	37.91	−0.11	15.551	15.58	−0.19	18.092	18.119	−0.15	2.0877	2.0923	−0.22	0.8609	0.8599	+0.12
EB72086	Elliot Bay	2	37.887	37.91	−0.06	15.583	15.58	+0.02	18.063	18.075	−0.07	2.0929	2.0974	−0.21	0.8627	0.8620	+0.08
EB72087	Elliot Bay	2	37.900	37.876	+0.06	15.587	15.57	+0.11	18.095	18.098	−0.02	2.0946	2.0928	+0.09	0.8613	0.8603	+0.12
EB72096	Elliot Bay	2	38.083	38.041	+0.11	15.628	15.605	+0.15	18.198	18.191	+0.04	2.0953	2.0912	+0.20	0.8588	0.8578	+0.12
BH2	Broken Hill	15	35.530	35.599	−0.19	15.384	15.37	+0.09	16.004	15.994	+0.06	2.2208	2.2258	−0.23	0.9613	0.9610	+0.03

* n = Number of analyses performed on each sample (average values shown). † Δ = Difference between ICP-MS and TIMS values.
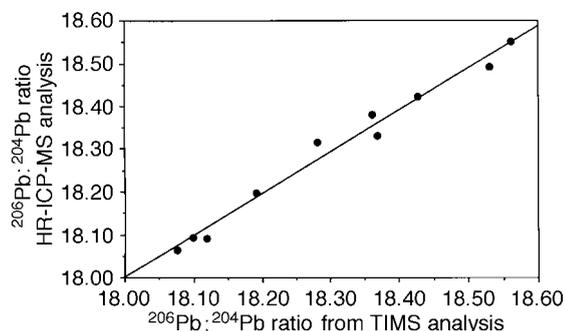
Fig. 2 Comparison between average $^{206}Pb/^{204}Pb$ ratio values obtained *via* HR-ICP-MS and TIMS techniques (for purposes of scale the Broken Hill galena sample has been omitted).

Comparison with TIMS values and accuracy of the analytical method

In order to study the accuracy of the present method, the Pb isotope ratios of 11 galena and galena-rich ore samples were measured by TIMS at CSIRO North Ryde and by HR-ICP-MS at the University of Tasmania. Samples were typically analysed 2–3 times by HR-ICP-MS, with the Pb concentration of the NIST SRM 981 external calibration standard and the unknown Pb sample being closely matched. Comparative data are given in Table 4. There is very good agreement between the two techniques and this is highlighted in Fig. 2, showing HR-ICP-MS values for the $^{206}Pb/^{204}Pb$ ratio plotted against TIMS data ($^{206}Pb/^{204}Pb_{HR-ICP-MS} = 0.98 \times {}^{206}Pb/^{204}Pb_{TIMS} + 0.45$, $r^2 = 0.983$ for $n = 10$). The ratio precision from HR-ICP-MS was about 0.05% and that from TIMS was about 0.02–0.05%.[15] A similar figure was presented in work by Date and Cheung[6] using an early model quadrupole ICP-MS. The difference in Pb ratio values between the two analytical techniques was generally less than $\pm 0.2\%$, and was in the range 0.001–0.1 for $^{208}Pb/^{204}Pb$, 0.004–0.03 for $^{207}Pb/^{204}Pb$, 0.003–0.04 for $^{206}Pb/^{204}Pb$, 0.001–0.008 for $^{208}Pb/^{206}Pb$ and 0.0001–0.004 for $^{207}Pb/^{206}Pb$.

Geological implications

Lead isotopes are powerful tools in exploration for mineral deposits and the investigation of problems of ore genesis.[4] However, unlike multi-element geochemical analyses, they are not commonly used when exploring for new deposits owing to the expense of TIMS analysis. From an earlier study,[4] the Cambrian volcanogenic massive sulfide (VMS) and post-Cambrian (Post C) mineralisation in Western Tasmania can be clearly separated when the Pb isotope ratio precision is less than ± 0.1 for $^{208}Pb/^{204}Pb$ and ± 0.05 for $^{207}Pb/^{204}Pb$ and $^{206}Pb/^{204}Pb$ (in terms of absolute ratio units). Our work has shown that Pb isotope ratios can be measured relatively quickly by HR-ICP-MS to a precision approaching that obtained by TIMS on the same mixed acid digestion solutions normally used in commercial geochemical analyses. This results in a reduction in cost when compared with TIMS measurements, and opens up the possibility of the routine use of Pb isotopes in geochemical exploration surveys for new mineral deposits.

CONCLUSION

This work has clearly shown that under routine operating conditions, precise and accurate Pb isotope ratios can be measured in Pb mineral concentrates using HR-ICP-MS. Based on the analysis of a series of standard reference solutions, this comparatively fast analytical method provided Pb ratios with precisions of 0.13% RSD or better for ratios to ^{204}Pb. For ratios to ^{206}Pb, the precisions obtained were of the order of 0.045%. TIMS and HR-ICP-MS were found to be in agreement to an accuracy of $\pm 0.2\%$, irrespective of the ratio considered. This level of accuracy is adequate for many geochemical applications. The relative ease and speed with which these values were obtained suggest that HR-ICP-MS may see increased use for geochemical Pb isotope ratio measurements.

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