



Reprint of "Comparison of datasets obtained by global-scale geochemical sampling in Australia, China and Europe"[☆]



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ABSTRACT

Catchment/floodplain sediment geochemical datasets from three continental-scale geochemical projects in Australia (AU), China (CH) and Europe (EU) were studied by comparing sample media, sample preparation, elements determined, analytical methods, detection limits and proportions of reportable values, and certified reference materials used. Twenty six elements (Ba, Ce, Co, Cr, Cu, Mo, Nb, Ni, Pb, Rb, Sr, Th, V, Y, Zn, Zr, Al₂O₃, CaO, K₂O, MgO, MnO, Na₂O, P₂O₅, SiO₂, Fe₂O₃ (total), TiO₂) were considered comparable among the 35 determined by all three projects, according to the criteria for global comparability of elements proposed in this paper. The median concentrations of all elements (except Co, Y, Zr, SiO₂ and TiO₂) in the three datasets increase in the following order: AU < EU ≤ CH, and the median CH/EU ratios for all elements range from 0.98 to 1.94, while the median CH/AU and EU/AU ratios for elements, such as CaO, Na₂O, MgO and Zn are generally greater than 2 (and up to 7), which could be explained partly by protracted weathering in Australia, and partly by the smaller grain size fraction analysed of the CH dataset (<1 mm) compared to AU and EU (<2 mm). In conclusion, a unified sample medium should be collected and unified sample preparation techniques should be followed. Key elements related to mineral resources and the environment should be determined and international or exchanged internal standard materials inserted in new national or global geochemical mapping projects in order to generate globally comparable datasets for establishing global geochemical baselines.

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1. Introduction

Ninety-four elements in the periodic table occur in nature, and their abundance in the Earth's upper continental crust has been studied for the past 120 years, beginning with the first estimation by Clarke (1889). Little is known, however, of their baseline concentrations and spatial distributions in the Earth's surface or near-surface environment (Wang et al., 2006). To know and to understand the current geochemical baselines are the first essential steps to quantify the future geogenic and human-induced changes, and to evaluate the past evolution due to geological processes (Darnley et al., 1995; Reeder, 2007; Smith et al., 2012; Wang, 2012; Zoback, 2001). Geochemical maps display the spatial distributions of chemical elements in Earth's surficial materials, facilitating the solution to problems related to natural primary resources, agriculture, forestry, environmental issues, human health, land use, and in many other fields (Darnley et al., 1995).

To date, a systematic geochemical mapping project covering the whole terrestrial surface of the Earth has not yet been carried out. Systematic regional geochemical mapping projects have been supported, however, by forward-thinking national governments and funds made available to state institutions to carry out this work. Since the 1970s, more than 50 countries have launched regional-scale geochemical mapping projects, covering a little over a fifth of the Earth's terrestrial surface (≈ 148,940,000 km²). Starting from the 1990s, since the implementation of IGCP 259 'International Geochemical Mapping' (1988–1992) and IGCP 360 'Global Geochemical Baselines' (1993–1997), significant progress has been made on global-scale or continental-scale geochemical mapping projects, covering a total area of approximately 32,000,000 km² in about 30 countries (≈ 22% of the Earth's land surface). Several valuable datasets have been generated to study continental-scale to global-scale geochemical patterns.

In order to establish a global geochemical database of permanent value, the report of IGCP 259 project outlined detailed recommendations and proposed the following seven basic requirements (Darnley et al., 1995):

- (1) commonly available representative sample media, collected in a standardised manner;
- (2) continuity of data across different types of landscape;

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- (3) adequate quantities of the designated sample media for future reference and research requirements;
- (4) analytical data for all elements of environmental or economic significance;
- (5) the lowest possible detection limits for all elements;
- (6) determination of the total amount of each element present, and
- (7) tight quality control at every stage of the process.

Several continental-scale geochemical surveys have been conducted in Australia, China, Europe, India, Mexico, and the United States, partly according to the recommendations of the IGCP 259 report (Darnley et al., 1995). However, analytical variation still exists in these datasets, because of different analytical techniques. Separating analytical variation from natural variation (resulting from lithology, geological or pedological process, climate, human activities, etc.) in a reliable way is crucial prior to application of the analytical data to global comparability.

Yao et al. (2011) compared analytical results generated in Chinese and European laboratories for the same sub-soil samples of FOREGS (Forum of European Geological Surveys, now EuroGeoSurveys) Geochemical Atlas of Europe project to evaluate between-laboratory bias. It was demonstrated that comparable analytical data of certain elements can be achieved by different laboratories and at different mapping stages. Reimann et al. (2012) selected elements with direct comparability from the NGS (National Geochemical Survey of Australia) and GEMAS (EuroGeoSurveys Geochemical Mapping of Agricultural and Grazing Land Soil project) based on exchanged standards analysed by both surveys. Reimann et al. (2012) concluded that to produce directly comparable datasets at the continental (or even country) scale is a difficult undertaking; they stated that even small differences in sample material, sampling method, sample preparation or analytical procedures can have a major impact on the observed element concentrations, and such effects have in the past often led to country borders being visible on geochemical maps rather than the true element spatial distribution patterns. According to these authors, the most crucial point appears to be analytical quality and the direct comparability of analytical results, and that total element concentrations are usually more comparable than values from a weaker extraction, such as aqua regia.

Nevertheless, for most completed and on-going continental/national-scale geochemical surveys, the between-laboratory bias has not been estimated (as Yao et al., 2011 did), and exchanged standard materials have not been analysed within the analytical stream of each project (as Reimann et al., 2012 did). How to assess the analytical variation among these datasets is a crucial issue that requires special attention.

In this study, six aspects including Sample media, Sample preparation, Elements determined, Analytical methods, Detection limits and proportions of reportable values, and Certified reference materials are considered in order to assess data comparability of three completed continental-scale geochemical mapping projects: the National Geochemical Survey of Australia (NGSA) (de Caritat and Cooper, 2011a), the Environmental Geochemical Monitoring Networks project of China (EGMON) (Cheng et al., 1997; Xie and Cheng, 1997; Xie et al., 1996, 1997), and the FOREGS Geochemical Baseline Mapping Programme in Europe (De Vos et al., 2006; Salminen et al., 1998, 2005).

2. Overviews of the three projects

2.1. The NGS project

The National Geochemical Survey of Australia (NGSA) project was conducted in collaboration with all State and Northern Territory geosciences agencies in Australia between 2006 and 2011 (Johnson, 2006). This project aimed to provide a pre-competitive geochemical database and to improve the national information of concentrations and abundances of energy-related elements, such as U and Th, by

determining the chemical composition of transported regolith samples from the outlet of large catchments (de Caritat and Cooper, 2011a).

Sampling was conducted from 2007 to 2009. The sampling method suitable to Australia landscape and climate conditions is described in detail in the NGS Field Manual (Lech et al., 2007). In total, 1186 catchments covering about 81% of Australia were sampled, representing an average density of approximately 1 site per 5200 km². Only six of the largest catchments were sampled at two widely separated locations, and 123 catchments (>10%) were sampled in duplicate for quality control purposes, totalling 1315 sample sites. At each site, two samples were collected: a Top Outlet Sediment (TOS) from 0 to 10 cm and a Bottom Outlet Sediment (BOS) from 60 to 80 cm on average. Both samples were taken as composite samples either from a shallow ~1 m² soil pit (TOS) or from generally at least 3 auger holes within an area of ~100 m² (BOS). The weight of each sediment sample was about 9 kg (de Caritat and Cooper, 2011a).

The parameters determined in the NGS project included total concentrations of 60 elements (the subject of this paper), aqua regia soluble concentrations of 60 elements, Mobile Metal Ion™ (MMI) concentrations of 54 elements, FeO, Loss On Ignition (LOI), pH (field and lab in 1:5 soil:water slurries), electrical conductivity (in 1:5 soil:water slurries), laser particle size analysis, and visible-near-infrared spectroscopy. All analytical methods are described in de Caritat et al. (2010) except for spectroscopy, which are in Viscarra Rossel et al. (2010, 2011).

For the generation of geochemical data of high quality and integrity, the NGS project followed a strict quality control programme involving randomised sample numbers, field duplicates, analytical replicates, internal standards and several certified reference materials. The quality control programme is discussed in the NGS Data Quality Assessment report (de Caritat and Cooper, 2011b).

2.2. The EGMON project

The Environmental Geochemical Monitoring Networks (EGMON) project in China was conducted from 1992 to 1997 with Professor Xie Xuejing as project leader. This project was part of the IGCP 259 (International Geochemical Mapping) pilot study to find a suitable sampling medium for continental-scale geochemical surveys, using a grid cell of 160 × 160 km². Floodplain sediment was tested as the first choice for a global sampling medium (Cheng et al., 1997; Xie and Cheng, 1997; Xie et al., 1996, 1997), following the successful results of the Western European Geological Surveys' project on Geochemical Mapping of Western Europe towards the Year 2000 conducted by the Working Group on Regional Geochemical Mapping under the leadership of Professor Bjørn Bølviken (Bølviken et al., 1990, 1993, 1996; Demetriades et al., 1990; Ottesen et al., 1989).

Floodplain sediments were taken from 532 sample sites covering the central and eastern part of China in 1994. The sampling sites were mostly located on the floodplains of large-catchment basins ranging from 1000 to 10,000 km² and at least 500–1000 m from the confluence point with other rivers. Two samples were taken at each site using a Luoyang shovel, i.e., (i) a surface floodplain sediment from a depth of 5–25 cm, and (ii) a deep floodplain sediment from a depth of 80–120 cm. Additional 314 stream/overbank sediment samples were collected at river beds in 1996 in Tibet plateau and Xinjiang province, where floodplain sediments are not developed. A total of 846 samples were taken in EGMON project to cover approximately 90% of China, corresponding to a sampling density of about 1 sample/10,000 km². The minimum weight of each sample was 2.5 kg (Cheng et al., 1997; Xie et al., 1996).

Total concentrations of 50 elements were determined in the EGMON project at the central laboratory of the Institute of Geophysical and Geochemical Exploration (Cheng et al., 1997; Xie et al., 1996); Pt and Pd were analysed at the central laboratory of the Henan Institute of Noble Metals, which is affiliated to the Ministry of Geology and Mineral Resources. The standard reference samples GSD 1–9 (Xie et al., 1985a),

GSS 1–8 (Xie et al., 1985b), and GAu 8–14 (Yan et al., 1995), Gpt 1–7 (Yan et al., 1998) were used for quality control (Cheng et al., 1997; Xie et al., 1996). The first two were recommended in the IGCP 259 report (Darnley et al., 1995) as two primary standard reference materials to be used in international geochemical mapping.

2.3. The FOREGS project

The FOREGS Geochemical Baseline Mapping Programme covering 26 European countries was launched in 1996. It is considered as the most famous continental-scale geochemical mapping project based on low-density sampling, following very closely IGCP 259 specifications (Darnley et al., 1995). Its main objectives were to apply standardised methods of sampling (Salminen et al., 1998), sample preparation, chemical analysis and data management for the compilation of a geochemical baseline database across Europe, and to use this reference network to level national baseline datasets (Salminen et al., 2005).

In the FOREGS project, samples of stream water, stream sediment, floodplain sediment and three types of soil (organic top soil, minerogenic top- and sub-soil) were collected during 1998–2001. The sampling procedures are described in the field manual (Salminen et al., 1998). Floodplain sediments, exclusively discussed in this paper, were sampled from the alluvial plain at the lowermost point (near to the outlet) of the large catchment basin (1000–6000 km²). The uppermost 25 cm of floodplain sediment was sampled from 790 sites. The weight of each sample was about 2 kg, enough to yield a minimum of 0.5 kg of <2 mm grain size sediment (Salminen et al., 2005).

In total, 54 parameters were measured on the floodplain sediment samples in five laboratories (Salminen et al., 2005). A strict quality control procedure was applied in sampling, sample preparation and chemical analysis of floodplain sediments to ensure the generation of analytical data of high quality and integrity. All participating laboratories had established quality control systems and estimated analytical uncertainty and sensitivity for all parameters. Two reference materials, ISE 921 and ISE 982, were analysed at regular intervals to monitor long-term stability and inter-laboratory comparison (Salminen et al., 2005).

3. Comparison of the three projects

The NGSa, EGMON and FOREGS (abbreviated by AU, CH and EU, respectively) projects were not strictly implemented according to the specifications of IGCP 259 (Darnley et al., 1995), but the sample media are consistent and geochemical datasets were generated under strict internal quality control during the sampling, sample preparation and analytical stages. Thus, comparability of the data is assumed possible for these three projects.

3.1. Media sampled

Floodplain sediments were used as sampling media in the CH and EU projects (Salminen et al., 1998; Xie et al., 1996). It is again noted that in the EU project, several types of sample media were collected, and only the floodplain sediment data are discussed in this paper. Catchment outlet sediments were collected by the AU project (see below).

A floodplain is an area of land adjacent to a stream or river that stretches from the banks of its channel to the base of the enclosing valley walls and experiences flooding during periods of high discharge. When a river overflows its banks during a flood event, it leaves behind layers of detritus (sand, silt, clay) when the water retreats. A catchment is a basin area drained by a river and its tributaries, and separated from adjacent catchments by drainage divides. The drainage network channels water and sediment through the catchment to a common outlet, where they are discharged to the next catchment. The transported regolith samples collected from the outlet of large catchments in the AU project are similar to floodplain sediments in most cases (de Caritat and Cooper, 2011a), but can include or even be dominated by aeolian material in very low relief areas. Thus, the analytical data of samples from floodplain sediments (CH and EU) and catchment outlet sediments (AU) are assumed similar and are compared in this paper.

3.2. Sample preparation

All samples in AU were prepared at Geoscience Australia and the detailed preparation protocols are discussed in the NGSa Sample Preparation Manual (de Caritat et al., 2009). After being air-dried and homogenised, each sample was split into two sub-samples, one for analysis and the other for storage and future investigation. The sub-sample for analysis was riffle split and dry sieved to <2 mm and <75 µm fractions. Before analyses, only <2 mm fraction was mechanically ground to <75 µm using a Rocklabs™ carbon steel bowl (164 mm outer diameter), lid, ring and puck assembly or head (CARB-200-BLRP) (de Caritat et al., 2009). In this paper, only <2 mm fraction in AU was discussed.

Each sample in CH was air-dried, then sieved to <1 mm for removing pebbles and plant residues, and stored in a glass bottle for future use. An analytical sample of 100 g was retrieved and ground to <74 µm in an agate ball mill, and then divided into four sub-samples following homogenisation (Xie et al., 1996).

All samples in EU were prepared in the laboratory of the Geological Survey of the Slovak Republic (GSSR). Floodplain sediment samples were dried at 40 °C, disaggregated in a porcelain mortar, passed through a 2 mm nylon sieve and split into two portions using a rotary divider; one was archived for further studies, and the other was pulverised in an agate disc mill to a grain size of <0.063 mm, homogenised and divided into five bottles and submitted to the analytical laboratories (Salminen et al., 2005).

Table 1
Comparison of elements determined and not determined^a by AU, CH and EU projects.

Projects	Elements determined	Elements not determined ^a
AU 2006–2011	59: Ag, As, Au, Ba, Be, Bi, Cd, Ce, Cl, Co, Cr, Cs, Cu, Dy, Er, Eu, F, Ga, Gd, Ge, Hf, Ho, La, Lu, Mo, Nb, Nd, Ni, Pb, Pd, Pr, Pt, Rb, S, Sb, Sc, Sm, Sn, Sr, Ta, Tb, Th, U, V, W, Y, Yb, Zn, Zr, Al ₂ O ₃ , CaO, Fe ₂ O ₃ (total), K ₂ O, MgO, MnO, Na ₂ O, P ₂ O ₅ , SiO ₂ , TiO ₂	12: B^b , Br, C , Hg , I, In, Li , N , Se , Te, Tl, Tm
CH 1992–1997	50: Ag, As, Au, B, Ba, Be, Bi, Cd, Ce, Co, Cr, Cu, F, Ga, Ge, Hg, I, La, Li, Mo, Nb, Ni, Pb, Pd, Pt, Rb, S, Sb, Sc, Se, Sn, Sr, Th, Tl, U, V, W, Y, Zn, Zr, Al ₂ O ₃ , CaO, Fe ₂ O ₃ (total), K ₂ O, MgO, MnO, Na ₂ O, P ₂ O ₅ , SiO ₂ , TiO ₂	21: Br, C , Cl , Cs, Dy, Er, Eu, Gd, Hf, Ho, In, Lu, N , Nd, Pr, Sm, Ta, Tb, Te, Tm, Yb
EU 1996–2005	54: As, Ba, Be, C, Cd, Ce, Co, Cr, Cs, Cu, Dy, Er, Eu, Ga, Gd, Hf, Hg, Ho, La, Li, Lu, Mo, Nb, Nd, Ni, Pb, Pr, Rb, Sb, Sm, Sn, Sr, Ta, Tb, Th, Tl, Tm, U, V, W, Y, Yb, Zn, Zr, Al ₂ O ₃ , CaO, Fe ₂ O ₃ (total), K ₂ O, MgO, MnO, Na ₂ O, P ₂ O ₅ , SiO ₂ , TiO ₂	17: Ag , Au , B , Bi , Br, Cl , F , Ge , I, In, N , Pd, Pt, S , Sc , Se , Te
All three projects	35: As, Ba, Be, Cd, Ce, Co, Cr, Cu, Ga, La, Mo, Nb, Ni, Pb, Rb, Sb, Sn, Sr, Th, U, V, W, Y, Zn, Zr, Al ₂ O ₃ , CaO, Fe ₂ O ₃ (total), K ₂ O, MgO, MnO, Na ₂ O, P ₂ O ₅ , SiO ₂ , TiO ₂	

^a Compared with the 71 elements required to be determined by the IGCP 259 project (see text).

^b Elements not analysed shown in bold belong to "List 1".

Table 2
Comparison of analytical methods of AU, CH and EU projects.

Projects	Laboratories	Analytical instruments	Decomposition techniques	Elements analysed
AU 2006–2011 (de Caritat et al., 2010)	Geoscience Australia	XRF	Oxidation (HBO ₂ /HBO ₂ and Li ₂ B ₄ O ₇ , LiNO ₃) + fusion (cellulose, NH ₄ l) + cooling to discs	Al ₂ O ₃ , CaO, Cl, Fe ₂ O ₃ (total), K ₂ O, MgO, MnO, Na ₂ O, P ₂ O ₅ , S, SiO ₂ , TiO ₂ Ag, As, Ba, Be, Bi, Cd, Ce, Co, Cr, Cs, Cu, Dy, Er, Eu, Ga, Gd, Ge, Hf, Ho, La, Lu, Mo, Nb, Nd, Ni, Pb, Pr, Rb, Sb, Sc, Sm, Sn, Sr, Ta, Tb, Th, U, V, W, Y, Yb, Zn, Zr Au, Pd, Pt
		Total ICP-MS	XRF discs + digestion (HF, HNO ₃)	
		FA ICP-MS	Fusion (PbO, Na ₂ CO ₃ , borax, SiO ₂) + oxidising fusion (Ag) + digestion (HNO ₃) + digestion (HCl)	
CH 1992–1997 (Xie et al., 1996)	Central laboratory of Institute of Geophysical and Geochemical Exploration	SIE	Fusion (Na ₂ O ₂) + dissolution (water)	F Ba, Co, Cr, Ga, Mn, Nb, Ni, P, Pb, Rb, S, Sc, Sr, Th, Ti, V, Y, Zn, Zr, Al ₂ O ₃ , CaO, Fe ₂ O ₃ (total), K ₂ O, MgO, Na ₂ O, SiO ₂ As, Sb, Bi, Hg, Se, Ge Ag, Au, Cd, Tl Cu, Li B, Be, Sn Ce, La, I, U Mo, W F
		XRF	Powder pellets	
		AFS	/	
		Flameless AAS	/	
		Flame AAS	/	
		AES	/	
		NAA	/	
		COL	/	
		POL	/	
		SIE	Fusion (NaOH) + dissolution (water) + digestion (citric acid)	
EU 1996–2005 (Salminen et al., 2005)	HINM	CES	/	Pd, Pt Ba, Cr, Rb, Sn, Sr, W, Y, Zn, Zr, Al ₂ O ₃ , CaO, Fe ₂ O ₃ (total), K ₂ O, MgO, MnO, P ₂ O ₅ , SiO ₂ , TiO ₂ As, Be, Cd, Ce, Co, Cs, Cu, Dy, Er, Eu, Ga, Gd, Hf, Ho, La, Li, Lu, Mo, Na ₂ O, Nb, Nd, Ni, Pb, Pr, Sb, Sm, Ta, Tb, Th, Tl, Tm, U, V, Yb Hg TOC
	BGS	XRF	Powder pellets	
	BRGM	Total ICP-MS	Fusion (Na ₂ O ₂) + digestion (HNO ₃)	
	MAFI	CV-AAS	/	
	GSSR	Special method	/	

Notation: BGS: British Geological Survey; BRGM: Bureau de Recherches Géologiques et Minières; FIG: Polish Institute of Geology; MAFI: Geological Survey of Hungary; GSSR: Geological Survey of the Slovak Republic; HINM: Henan Institute of Noble Metals.

AAS: atomic absorption spectrometry; AES: atomic emission spectrometry; AFS: atomic fluorescence spectrometry; COL: colourimetry; CES: chemical emission spectrometry; CV: cold vapour; FA: fire assay; AR: aqua regia; ICP-MS: inductively coupled plasma mass spectrometer; NAA: neutron activation analysis; POL: polarography; SIE: selective ion electrode; XRF: X-ray fluorescence spectrometry. Special method: TOC, total organic carbon was determined by a pyrolysis technique with non-dispersive infrared detection using a Dohrmann-Rosemount DC-190 (USA) carbon analyser (Salminen et al., 2005).

Element concentration levels in samples vary with grain size analysed. To ensure comparability, all the samples should be sieved to the same size fraction and then ground prior to chemical analysis. However, the grain size fraction sieved in CH (<1 mm) is finer than AU (<2 mm) and EU (<2 mm), and the grain size ground prior to chemical analysis in EU (<63 µm) is finer than AU (<75 µm) and CH (<74 µm). The variation among AU, CH and EU from grain size fraction will be discussed in Section 4.2.

3.3. Elements determined

The IGCP 259 project recommended 71 elements to be determined, which are divided by Darnley et al. (1995) into a high priority “List 1” (51 elements: Ag, As, Au, B, Ba, Be, Bi, C, Cd, Ce, Cl, Co, Cr, Cs, Cu, F, Ga, Ge, Hg, I, La, Li, Mo, N, Nb, Ni, Pb, Rb, S, Sb, Sc, Se, Sn, Sr, Th, U, V, W, Y, Zn, Zr, Al₂O₃, CaO, Fe₂O₃ (total), K₂O, MgO, MnO, Na₂O, P₂O₅, SiO₂, TiO₂), and a lower priority but potentially important “List 2” (20 elements: Br, Dy, Er, Eu, Gd, Hf, Ho, In, Lu, Nd, Pd, Pr, Pt, Sm, Ta, Tb, Te, Tl, Tm, Yb).

Table 1 lists the elements determined and not determined by the AU, CH and EU projects in comparison with the above 71 elements recommended to be analysed by the IGCP 259 project. Thirty five elements are common to all three projects: As, Ba, Be, Cd, Ce, Co, Cr, Cu, Ga, La, Mo, Nb, Ni, Pb, Rb, Sb, Sn, Sr, Th, U, V, W, Y, Zn, Zr, Al₂O₃, CaO, Fe₂O₃ (total), K₂O, MgO, MnO, Na₂O, P₂O₅, SiO₂, and TiO₂, all of which belong to “List 1”. Elements not determined by any of the three projects are Br, In, N and Te, which fall within “List 2” except for N. A number of elements of economic (e.g., Au, Ag, Pt, Pd in EU project) and environmental (e.g., Hg in AU project) significance were not analysed by total methods. Carbon and N were not determined by the three projects (except C in EU project), even though they are included in “List 1”.

3.4. Analytical methods

The analytical instruments used in the three projects are listed in Table 2. The decomposition techniques are shown in Table 2 for XRF, ICP-MS and SIE (these instruments were used at least in two projects). Most elements of AU and EU projects were determined by XRF and total digestion ICP-MS. The more complicated instruments, including several traditional techniques like Polarography (Mo, W) and Colourimetry (I, U), were used in the CH project conducted 20 years ago (1992–1997). All ten major elements were measured by XRF for AU, CH and EU projects. The samples were similarly prepared for XRF in CH and EU projects.

In continental-scale projects, where a large number of samples are collected, a sensitive, rapid and economical analytical protocol is needed. The use of different analytical methods and/or laboratories for the determination of the same element could result in bias in the geochemical datasets. Therefore, all samples should be analysed for the same suite of elements in the same laboratory and by the same analytical technique to ensure the generation of analytical results of high quality. However, this category is unrealistic, and the alternative method is that analysing the same certified materials in different projects could control the variation resulting from different laboratories, instruments or decomposition techniques.

3.5. Detection limits and proportions of reportable values

The detection limits (DLs), particularly of trace elements, should be below or significantly below presently estimated crustal abundances (Darnley et al., 1995). Table 3 shows three widely quoted versions of continental crustal abundances (columns 2–4) (Taylor and McLennan, 1985,

Table 3
Analytical DLs and reportable proportions of samples from the AU (N = 1315), CH (N = 846) and EU (N = 790) projects.

Elements	Continental crustal abundance			Suggested DLs	DLs			Reportable proportions (%)		
	2	3	4		5	AU	CH	EU	AU	CH
1	2	3	4	5	6	7	8	9	10	11
Ag	0.08	0.07	0.055	0.02	0.03	0.02	/	1	100	/
As	1	1.7	2.4	0.5–1.0	0.4	0.5	1	98	100	95
Au	0.003	0.0025	0.0009	0.0002	0.001	0.0002	/	93	100	/
B	10	11	11	/	/	1	/	/	100	/
Ba	250	584	620	/	0.5	50	3	100	100	100
Be	1.5	2.4	1.4	0.5	1.1	0.5	0.02	71	99	99
Bi	0.06	0.085	0.15	0.05–0.1	0.02	0.1	/	97	99	/
Br	/	1	(0.25)	/	/	/	/	/	/	/
C total	/	1900	(3800)	/	/	/	/	/	/	/
Cd	0.098	0.1	0.082	0.05–0.1	0.1	0.01	0.02	42	100	99
Ce	33	60	57	/	0.03	3	0.02	100	100	100
Cl	/	472	112	/	10	/	/	99	/	/
Co	29	24	19	/	0.1	2	2	100	100	94
Cr	185	126	76	/	0.5	7	3	100	100	100
Cs	1 (1.5)	3.4	2	/	0.1	/	4	100	/	87
Cu	75	25	26	/	0.2	2	1	99	100	100
Dy	3.7	3.8	3.7	/	0.1	/	0.02	100	/	100
Er	2.2	2.1	2.2	/	0.03	/	0.02	100	/	100
Eu	1.1	1.3	1.3	0.5–1.0	0.03	/	0.02	99	/	100
F	/	525	540	/	20	100	/	100	100	/
Ga	18	15	19	/	0.1	2	1	100	100	100
Gd	3.3	4	4.3	/	0.03	/	0.02	100	/	100
Ge	1.6	1.4	1.2	0.5–1.0	0.04	0.1	/	99	100	/
Hf	3	4.9	4.5	1.2	0.04	/	0.05	100	/	100
Hg	/	0.04	0.007	0.01–0.05	/	0.002	0.0001	/	100	100
Ho	0.78	0.8	0.77	1	0.02	/	0.02	100	/	100
I	/	0.8	(0.07)	0.2–0.5	/	0.5	/	/	87	/
In	0.05	0.05	0.045	0.05–0.1	/	/	/	/	/	/
La	16	30	29	/	0.1	16	0.02	100	95	100
Li	13	18	17	/	/	3	0.05	/	100	100
Lu	0.3	0.35	0.33	/	0.02	/	0.02	99	/	100
Mo	1	1.1	0.5	0.5	0.3	0.3	0.05	88	96	100
N	/	60	60	/	/	/	/	/	/	/
Nb	11 (8)	19	10	/	0.03	5	1	100	100	100
Nd	16	27	26	/	0.1	/	0.02	100	/	100
Ni	105	56	31	/	0.5	2	1	100	100	100
Pb	8	14.8	15	/	0.1	5	1	100	100	100
Pd	0.001	0.0004	0.00075	0.0005	0.001	0.0001	/	48	100	/
Pr	3.9	6.7	6.5	/	0.02	/	0.02	100	/	100
Pt	/	0.0004	0.0008	0.001	0.0005	0.0001	/	48	100	/
Rb	32 (37)	78	70	/	0.2	5	1	100	100	100
S	/	697	250	/	10	100	/	100	92	/
Sb	0.2	0.3	0.18	0.04	0.4	0.2	0.02	35	99	98
Sc	30	16	17	/	0.3	4	/	100	97	/
Se	0.05	0.12	0.07	0.02	/	0.01	/	/	100	/
Sm	4.9	5.3	4.9	/	0.04	/	0.02	98	/	100
Sn	2.5	2.3	1.4	1.2	0.2	1	1	98	94	70
Sr	260	333	350	/	0.2	10	1	100	100	100
Ta	1 (0.8)	1.1	0.65	1	0.02	/	0.05	99	/	100
Tb	0.6	0.65	0.69	/	0.02	/	0.02	99	/	100
Te	/	5	(0.006)	0.01–0.02	/	/	/	/	/	/
Th	3.5	8.5	6	/	0.02	3	1	100	100	100
Tl	0.36	0.52	0.42	0.1–0.5	/	0.1	0.02	/	100	98
Tm	0.32	0.3	0.34	0.5	/	/	0.02	/	/	100
U	0.91	1.7	1.3	0.05	0.02	1	1	100	99	69
V	230	98	112	/	0.1	15	2	100	99	99
W	1	1	0.6	0.2–0.5	0.1	0.5	0.05	97	99	99
Y	20	24	17	/	0.05	10	0.02	100	98	100
Yb	2.2	2	0.69	/	0.04	/	0.02	100	/	100
Zn	80	65	76	/	0.9	10	1	99	100	100
Zr	100	203	160	/	0.2	10	1	100	100	100
Al ₂ O ₃	8.41%	7.96%	7.85%	/	0.005%	0.1%	0.1%	100	100	100
CaO	5.29%	3.85%	3.84%	/	0.002%	0.1%	0.05%	100	100	100
Fe ₂ O ₃ total	7.07%	4.32%	4.58%	/	0.005%	0.1%	0.01%	100	100	100
K ₂ O	0.91%	2.14%	1.92%	/	0.005%	0.1%	0.05%	100	100	100
MgO	3.20%	2.2%	1.9%	/	0.01%	0.1%	0.1%	98	100	87
MnO	0.18%	0.09%	0.10%	/	0.005%	0.004%	0.01%	96	100	99
Na ₂ O	2.30%	2.36%	2.55%	/	0.01%	0.1%	0.2%	99	100	99
P ₂ O ₅	/	0.17%	0.17%	/	0.005%	0.023%	0.01%	100	100	100
SiO ₂	26.80%	28.8%	28.33%	/	0.01%	0.1%	0.1%	100	100	100
TiO ₂	0.9%	0.67%	0.67%	/	0.005%	0.017%	0.005%	100	100	100

Table 4
Comparison of CRMs and the uncertified elements in CRMs for AU, CH and EU projects.

Projects	CRMs	Elements not certified in CRMs
AU	TILL-1, TILL-2, TILL-3, LKSD-1, STSD-3	Ag, Bi, Cd, Cl, Dy, Ga, Gd, Ge, Ho, Pd, Pr, Pt, S, Sn
CH	GSD 1–9, GSS 1–8, GAu 8–14, GPt 1–7	/
EU	ISE 921, ISE 982	Dy, Er, Eu, Gd, Hf, Ho, Lu, Pr, Sm, Ta, Tb, Tm

TILL-1, TILL-2, TILL-3, LKSD-1, STSD-3 are from Natural Resources Canada. Certificates of Analysis could be found in website: <http://www.nrcan.gc.ca/minerals-metals/technology/3631>.

GSD 1–9 (Xie et al., 1985a), GSS 1–8 (Xie et al., 1985b), GAu 8–14 (Yan et al., 1995), GPt 1–7 (Yan et al., 1998).

ISE 921 and ISE 982 were produced by the Wageningen Evaluating Programmes for Analytical Laboratories. Their Certificates of Analysis are shown in <http://www.lgcstandards.com/WebRoot/Store/Shops/LGC/FilePathPartDocuments/ST-WB-CERT-1067131-1-1-1.PDF> and <http://www.wepal.nl/website/downloads/RefMatISE.htm>, respectively.

1995; Wedepohl, 1995; Yan and Chi, 1997, 2005), and suggested DLs (column 5) for elements with crustal abundances below 3 mg/kg (Darnley et al., 1995). The DLs of Ag, Au, Be, Cd, Pd and Sb for AU, Bi, I, La, Sb, U and W for CH, and As, Cs and U for EU are above the suggested DLs (for elements with crustal abundances below 3 mg/kg) or crustal abundance values given by the above-quoted authors (for other elements).

Proportions of reportable values indicate the ratio of the number of samples falling above the detection limit to the total number of samples. Taking 80% as the cut-off value (Darnley et al., 1995), the results (columns 9–11 in Table 3) are not satisfactory for Ag, Be, Cd, Pd, Pt and Sb in AU, and Sn and U in EU projects. The proportions of reportable values for all elements are above 80% in the CH project.

3.6. Certified reference materials (CRMs) used

Analytical quality control includes international or inter-laboratory bias monitored by certified reference materials (CRMs), and the routine between-batch drift within a laboratory is usually controlled by laboratories' own procedures (Darnley et al., 1995). All the participating laboratories of these three projects have established strict analytical quality control. Thus, the errors between batches within a laboratory are assumed acceptable. The bias among different laboratories is the greatest problem to be solved for comparability.

The uncertainty of data can be defined by two important types of error, precision and accuracy, which can be documented by analysing CRMs regularly within sample batches. Precision, also called reproducibility, is the degree of closeness to which repeated analyses of CRMs agree with each other. Accuracy is the degree of closeness of the average analytical results of CRMs to their certified values (Greenberg et al., 1992). Table 4 shows the international CRMs used in these three projects. Only the AU project in Australia reported the resulting quality control statistics (de Caritat and Cooper, 2011b), thus making it difficult to quantitatively compare quality control among these three projects. Comparing the elements analysed in projects with ones certified

in the inserted CRMs could partially assess the quality of resulting datasets.

Five certified reference materials (TILL-1, TILL-2, TILL-3, LKSD-1, STSD-3) were covertly inserted in the analytical batches of the AU project to help quantify analytical precision and accuracy (de Caritat and Cooper, 2011b). However, among the 59 elements analysed, the contents of Ag, Bi, Cd, Cl, Dy, Ga, Gd, Ge, Ho, Pd, Pr, Pt, S and Sn in CRMs were not certified. In the EU project, two CRMs (ISE 921, ISE 982) were analysed at regular intervals to monitor long-term stability, and to enable comparison of data from different methods and different laboratories (Salminen et al., 2005). However, among 54 elements analysed in the EU project, standardised values in two CRMs (ISE 921, ISE 982) for Dy, Er, Eu, Gd, Hf, Ho, Lu, Pr, Sm, Ta, Tb and Tm are not available. Four CRMs (GSS, GSD, GAu, GPt) were used for quality control in the CH project (Xie et al., 1996) and the values of all elements determined have been certified.

4. Results and discussion

4.1. Criteria for selecting elements for comparison

Seven criteria for selecting elements for comparison to establish a global geochemical baselines database proposed in this paper are:

- (1) Representative samples of a unified sampling medium should be collected in a standardised manner;
- (2) All the samples should be sieved to the same size fraction and then ground prior to chemical analysis;
- (3) Elements selected for dataset comparability should be determined by all projects (elements of environmental and economic significance should be included);
- (4) Total element contents should be determined by well-established analytical methods;
- (5) Detection limits should be lower than the suggested values given by IGCP 259/360 or lower than crustal abundance values;
- (6) Proportions of reportable values above DLs for each element should be over 80%; and
- (7) Certified reference materials (CRMs) should be inserted in the analytical batches at regular intervals, and the reported CRM values should be certified for all element selected in criteria (2) above.

Twenty six elements (Ba, Ce, Co, Cr, Cu, Mo, Nb, Ni, Pb, Rb, Sr, Th, V, Y, Zn, Zr, Al₂O₃, CaO, Fe₂O₃ (total), K₂O, MgO, MnO, Na₂O, P₂O₅, SiO₂, TiO₂) out of the 35 elements determined by all three projects met these conditions.

Yao et al. (2011) and Reimann et al. (2012) have studied comparability of analytical results, produced in different laboratories and in different mapping projects. Table 5 lists the elements selected and methods used to investigate comparability by the aforementioned authors, and this study.

Based on the results of exchanged internal standards analysed by two continental-scale soil surveys in Europe (GEMAS) and Australia (NGSA), total concentration of 26 elements (As, Ba, Ce, Co, Cr, Ga, Nb,

Notes to Table 3:

The units of data are in mg/kg, except those indicated with %.

Elements (column 1) – including all elements required to be determined according to the Final Report of IGCP Project 259 (Darnley et al., 1995).

Column 2 – Continental Crust (Taylor and McLennan, 1985, 1995, values in brackets are after McLennan, 2001);

Column 3 – Continental Crust (Wedepohl, 1995);

Column 4 – Continental Crust in the eastern part of China (Yan and Chi, 1997, 2005, Results in brackets are reference values).

Suggested DL: Detection limits of elements with crustal abundances below 3 mg/kg, suggested in Final Report of IGCP Project 259 (Darnley et al., 1995).

Numbers with underline indicate that detection limits are not satisfactory.

Numbers in bold indicate that reportable percentage proportion of samples is below 80%.

Table 5
Elements selected and methods used to study data comparability by Yao et al. (2011), Reimann et al. (2012), and this study.

Source	Elements selected to be comparable	Methods used to study data comparability
Reimann et al. (2012)	26: As, Ba, Ce, Co, Cr, Ga, Nb, Ni, Pb, Rb, Sr, Th, V, Y, Zn, Zr, Al ₂ O ₃ , CaO, K ₂ O, Fe ₂ O ₃ (total), MgO, MnO, Na ₂ O, P ₂ O ₅ , SiO ₂ , TiO ₂	Internal project standards were exchanged and inserted in the analytical batches of each project.
Yao et al. (2011)	23 (without bias): As, Ba, Co, Cr, Ga, Gd, Mn, P, Pb, Rb, Sc, Sr, Th, Ti, U, Y, Zr, Al ₂ O ₃ , CaO, Fe ₂ O ₃ (total), MgO, Na ₂ O, SiO ₂ 21 (with slight between-laboratory bias): Ce, Cu, Dy, Er, Eu, Hf, Ho, K ₂ O, La, Lu, Nb, Nd, Ni, Pr, S, Sm, Ta, Tb, Tl, Tm, Yb	All samples from different projects were analysed in different laboratories. For example, the composite sub-soil samples from the FOREGS project were analysed by European and Chinese laboratories.
This paper	26: Ba, Ce, Co, Cr, Cu, Mo, Nb, Ni, Pb, Rb, Sr, Th, V, Y, Zn, Zr, Al ₂ O ₃ , CaO, K ₂ O, Fe ₂ O ₃ (total), MgO, MnO, Na ₂ O, P ₂ O ₅ , SiO ₂ , TiO ₂	Six criteria: (1) sample media, (3) sample preparation, (3) elements determined, (4) analytical methods, (5) detection limits and proportions of reportable values, and (6) certified reference materials, were used to evaluate data comparability for completed projects.

Ni, Pb, Rb, Sr, Th, V, Y, Zn, Zr, Al₂O₃, CaO, Fe₂O₃ (total), K₂O, MgO, MnO, Na₂O, P₂O₅, SiO₂, TiO₂) delivered comparable results (Reimann et al., 2012). When comparing these elements with the 26 selected in this paper, the differences occur exclusively for Cu(+), Mo(+), As(−) and Ga(−), where postscript (+) indicates an element selected here but not in Reimann et al. (2012), and (−) the opposite. Reimann et al. (2012) selected two criteria for direct comparability between the GEMAS and NGSAs projects, i.e., (1) that the average (arithmetic mean) results from the two projects differed from one another by less than 25% for all of the available project standards, and (2) that the averages were above the lower limit of detection for the analyte. Copper and Mo did not meet the first criterion and were removed from the comparison dataset. Arsenic and Ga was excluded in this study, because the DL of As for EU are not below the suggested DLs, and certified values of Ga are unavailable in the CRMs used in the NGSAs project.

The analytical data produced in the IGGE central laboratory on 190 composited sub-soil samples from the FOREGS project, and the

FOREGS average values of samples in each Global Reference Network grid, were compared by Yao et al. (2011). The scatter diagram for the pair determinations was used to visually estimate the variation between IGGE and FOREGS laboratories. In the scatter diagrams, the data of 23 elements (Table 5) fall along a generally straight line (the 45° diagonal) showing that no systematic errors exist between the two datasets, and the data fall along a straight line but off the diagonal for 21 elements (Table 5) which show slight between-laboratory bias (Yao et al., 2011). In this paper, all the selected 26 elements, except Mo, V and Zn, fall within the aforementioned list of 44 elements (Table 5; Yao et al., 2011). Molybdenum, V and Zn were not included in the Yao et al. (2011) list, because obvious biases between IGGE and FOREGS datasets exist at values near detection limits (Yao et al., 2011). All 26 elements selected by Reimann et al. (2012), except V and Zn, are included in the above 44 elements list.

Elements with good comparability picked out by the three methods (Reimann et al., 2012; Yao et al., 2011; this study) are strikingly similar

Table 6
Comparison of statistical parameters of analytical results from the AU, CH and EU projects.

Element	25th percentile			Median			75th percentile			Power (100%)/power (95%)			Median ratio			IQR		
	AU	CH	EU	AU	CH	EU	AU	CH	EU	AU	CH	EU	CH/AU	CH/EU	EU/AU	AU	CH	EU
<i>Trace elements – mg/kg</i>																		
Ba	199	393	248	315.1	488	379	411.7	591	526.5	2.9/1.2	1.6/0.6	2.5/1.0	1.55	1.29	1.2	212.7	198	278.5
Ce	23.21	49	34.61	42.1	63	50.2	57.17	80	68.15	2.5/1.1	1.3/0.7	2.1/1.0	1.5	1.25	1.19	33.96	31	33.54
Co	3.4	8	4	8.3	10.6	7	13.3	13	11.5	2.9/1.6	1.9/0.7	1.8/1.4	1.28	1.51	0.84	9.9	5	7.5
Cr	31.9	47	35	48	64	59	66.5	80	87.5	2.6/1.1	2.0/0.9	2.7/1.5	1.33	1.08	1.23	34.6	33	52.5
Cu	7.2	15.1	11	13.5	21.1	17	20.7	27.3	28	2.9/1.4	1.9/0.9	2.4/1.4	1.56	1.24	1.26	13.5	12.2	17
Mo	0.3	0.5	0.4	0.5	0.63	0.62	0.8	0.89	1.01	1.8/0.8	1.4/0.9	3.9/1.2	1.26	1.02	1.24	0.5	0.39	0.61
Nb	5.2	10.9	7	8.5	14	10	11.4	17	13	3.3/1.0	1.2/0.6	2.4/0.9	1.65	1.4	1.18	6.2	6.1	6
Ni	9.4	17.15	12	15.3	25	22	22.7	32	33	2.7/1.2	2.7/1.0	2.7/1.6	1.63	1.14	1.44	13.3	14.85	21
Pb	8.37	18	15	12.86	23	22	17.35	30	35	3.5/1.1	1.9/0.8	3.2/1.4	1.79	1.05	1.71	8.98	12	20
Rb	29.8	78.5	46.5	51.7	93	71	77.7	115	97	3.1/1.4	1.4/0.6	1.9/1.0	1.8	1.31	1.37	47.9	36.5	50.5
Sr	38.2	108.5	80.5	68.3	164	131	113.8	224.5	203	3.8/1.7	1.8/1.0	2.0/1.2	2.4	1.25	1.92	75.6	116	122.5
Th	5.46	8.2	5	7.89	11.3	8	11.21	14.3	11	2.7/1.0	1.5/1.0	1.9/1.0	1.43	1.41	1.01	5.75	6.1	6
V	31.3	57	34	54.6	74	56	82.8	94	81	3.8/1.2	1.7/0.8	2.4/1.3	1.36	1.32	1.03	51.5	37	47
Y	12	18.28	14.7	21.1	24	20.1	28.9	29	26.8	2.0/1.1	0.9/0.6	1.8/0.9	1.14	1.19	0.95	16.9	10.72	12.1
Zn	13.2	50	42	31	65	65	52.2	86	102	2.4/1.8	2.5/0.8	2.9/1.5	2.1	1	2.1	39	36	60
Zr	215.7	175	152.5	305.3	237	215	394.5	293.5	283	2.6/0.9	1.2/0.7	1.6/0.9	0.78	1.1	0.7	178.8	118.5	130.5
<i>Major elements – wt.%</i>																		
Al ₂ O ₃	4.54	10.04	6.4	8.06	11.85	10.4	11.12	13.7	12.9	2.2/1.1	1.0/0.5	2.5/1.2	1.47	1.14	1.29	6.57	3.66	6.50
CaO	0.19	1.25	0.84	0.44	3.12	2.07	0.91	6.65	6.82	3.2/2.4	2.4/1.8	3.1/2.3	7.02	1.51	4.66	0.72	5.40	5.98
*Fe ₂ O ₃ T	2.02	3.39	2.12	3.2	4.2	3.33	4.61	5.16	4.53	2.5/1.0	1.3/0.7	2.2/1.1	1.31	1.26	1.04	2.59	1.77	2.41
K ₂ O	0.66	1.98	1.44	1.2	2.28	2	1.77	2.6	2.62	2.9/1.6	1.2/0.5	1.7/0.9	1.91	1.14	1.67	1.11	0.62	1.18
MgO	0.16	0.99	0.5	0.5	1.49	1.2	0.91	2.17	2	3.0/2.4	1.8/0.9	2.5/2.2	3.01	1.25	2.42	0.74	1.18	1.50
MnO	0.02	0.05	0.05	0.04	0.07	0.07	0.07	0.09	0.1	2.1/1.5	2.0/0.8	3.5/1.2	1.66	1.01	1.65	0.06	0.04	0.06
Na ₂ O	0.11	0.93	0.4	0.31	1.55	0.8	0.69	2.06	1.5	2.8/2.3	1.9/1.2	1.9/1.5	5.07	1.94	2.61	0.58	1.13	1.10
P ₂ O ₅	0.04	0.09	0.07	0.06	0.13	0.11	0.1	0.15	0.17	1.7/1.1	1.2/0.7	2.4/1.3	2.05	1.14	1.81	0.06	0.06	0.10
SiO ₂	69.37	58.66	55.2	77.82	63.45	64.6	87.86	68.35	72	2.1/0.3	0.7/0.3	1.1/0.5	0.82	0.98	0.83	18.49	9.69	16.80
TiO ₂	0.34	0.47	0.31	0.58	0.62	0.48	0.8	0.77	0.67	2.5/1.0	1.5/0.7	1.6/1.0	1.07	1.3	0.82	0.46	0.31	0.36

Notation: AU – NGSAs project in Australia (N = 1315, top catchment outlet sediments, <2 mm); CH – EGMON project in China (N = 846, top floodplain sediments, <1 mm); EU – FOREGS project in Europe (N = 790, top floodplain sediments, <2 mm); power (100%) = log (max) – log (min); power (95%) = log (97.5th percentile) – log (2.5th percentile); IQR (inter-quartile range) = 75th percentile–25th percentile; *Fe₂O₃T – Fe₂O₃ (total).

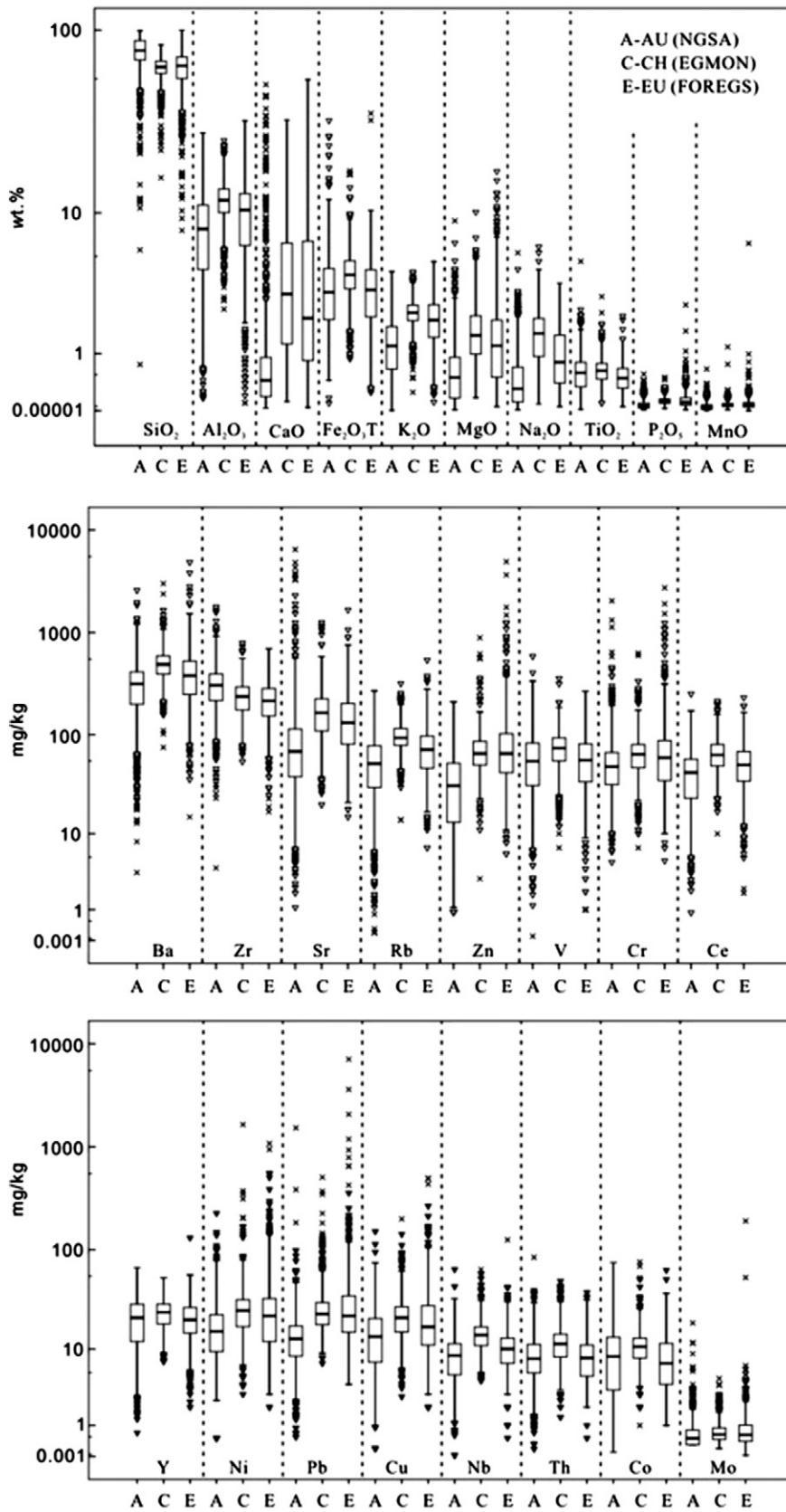


Fig. 1. Boxplot comparison of AU, CH and EU datasets. Box length represents the inter-quartile range (25th to 75th percentiles) and contains the median (thick black line). Triangles: cases with values between 1.5 and 3 times box length (inter-quartile range) from the upper or lower edge of the box; Crosses: cases with values more than 3 times box length from the upper or lower edge of the box (Tukey, 1977).

(Table 5). The most likely explanations are: (1) the analytical methods used for the above-mentioned comparable elements are technically similar, for example XRF, (2) laboratories participating in the projects belong to the world-leading class level, and (3) the projects were conducted under strict quality control procedures at each stage from sampling to analysis.

All elements could be globally comparable if the geochemical mapping projects were strictly conducted under the specifications set by IGCP 259 (Darnley et al., 1995). However, it is difficult for all projects to meet all the requirements due to limited funds, time, laboratory capability, and personnel during implementation of the projects. Inserting exchanged internal standard materials in the analytical stream of each continental-scale project (Reimann et al., 2012) is economical and easily implemented, and is strongly recommended to be used for between-project/laboratory comparability in the future. The criteria proposed in this paper possibly could be used for selecting datasets from the tremendous amount of data already accumulated by national- and continental-scale geochemical mapping projects where international or exchanged internal project standards have not been analysed.

4.2. Statistical comparison of datasets for 26 elements with good comparability

Table 6 shows a statistical overview of the analytical data from the AU, CH and EU projects for the 26 elements found to be comparable. Several descriptive statistical parameters are summarised in Table 6, including 25th percentile, median, 75th percentile, power (100%) (= $\log(\max) - \log(\min)$), power (95%) (= $\log(97.5\text{th percentile}) - \log(2.5\text{th percentile})$) and median ratio.

For geochemical data, the median value is a robust estimator of the central tendency (Reimann et al., 2008) and, since it is not seriously affected by extreme values, can be used for comparisons. All 26 elements, except Zr and SiO₂, show higher medians in the CH project than in the AU project, particularly for CaO, Na₂O, MgO, Sr, Zn, and P₂O₅ (in decreasing order of median ratio), for which median values in the CH dataset are significantly above (>factor 2) the corresponding values in the AU project. The medians of all elements, except Zn and SiO₂, are higher in the CH project than in the EU project, and all the CH/EU median ratios range from 0.98 (SiO₂) to 1.94 (Na₂O). Zinc and SiO₂ show nearly the same medians in both CH and EU datasets (65 and 65 mg/kg, and 63.45 and 64.60%, respectively). Medians of most elements in the EU project are much above those in the AU project, except for Co, Zr, SiO₂ and TiO₂. Elements in the EU project with more than twice the median value of the AU project are (in decreasing order of median ratio): CaO, Na₂O, MgO and Zn; the Y medians are nearly similar in these two datasets (20.1 and 21.1 mg/kg). The highest and lowest median values of most elements, except Co, Y, Zr, TiO₂ and SiO₂, are recorded in the CH and AU projects, respectively. For all elements, except Zr and SiO₂, the Chinese floodplain sediments have the highest 25th percentile, and for all elements, except Th, Zr, SiO₂ and TiO₂, the Australian catchment outlet sediments have the lowest 25th percentile. The 75th percentiles of different projects vary significantly from element to element (Table 6).

Power (100%) shows the order of magnitude of variation between maximum and minimum of a dataset. This statistical parameter, however, reflects only a characteristic of the dataset and not of the study area, partly because element concentrations reported below DLs are converted to one or one half DL (usually recorded as minima), and partly for the reason that the maximum values are probably attributed to poor representativeness of samples during sampling or analysis process. Hence, both minimal and maximal element concentrations are not authentic responses of the study area. Power (95%) is the order of magnitude variation between 97.5th percentile and 2.5th percentile; the confidence interval, 2.5%–97.5%, could improve the robustness and validity of datasets. Elements with a power (100%) value larger than 3 in the AU dataset are (in order of decreasing value): Sr (3.8), V (3.8), Pb (3.5),

Nb (3.3), CaO (3.2), Rb (3.1) and MgO (3.0), and in the EU dataset: Mo (3.8), MnO (3.5), Pb (3.2) and CaO (3.1). All power (100%) values for the CH project are less than 3 (range: 0.7 (SiO₂)–2.7 (Ni)). The values of power (95%) for the AU, CH and EU datasets are from 0.3 (SiO₂) to 2.4 (CaO, MgO), 0.3 (SiO₂) to 1.8 (CaO) and 0.5 (SiO₂) to 2.3 (CaO), respectively.

Fig. 1 visually displays the statistical distribution of 26 elements from the three datasets (AU, CH, EU) in the form of boxplots. Box lengths represent the inter-quartile ranges (IQRs, 75th percentile–25th percentile), which are also listed in Table 6. In the AU project, elements with the largest IQR are Ce, Co, V, Y, Zr, Nb, Fe₂O₃ (total), TiO₂, SiO₂ and Al₂O₃, and with the smallest IQR are Ni, Pb, Sr, Th, CaO, MgO and Na₂O. In the CH project, elements with the largest IQR are Th and Na₂O, and with the smallest are Ba, Cr, Cu, Mo, Rb, Zn, Ce, Co, V, Y, Zr, Al₂O₃, K₂O, MnO, P₂O₅, SiO₂, Fe₂O₃ (total) and TiO₂. In the EU dataset, elements with the largest inter-quartile range are Mo, Ni, Pb, Sr, Ba, Cr, Cu, Rb, Zn, CaO, K₂O, MgO, MnO and P₂O₅, while only Nb has the smallest IQR.

The medians of most elements in the three datasets are in the order CH > EU > AU, except Co, Y and TiO₂ (CH > AU > EU), Zr (AU > CH > EU), and SiO₂ (AU > EU > CH). The differences existing between CH and EU are significantly smaller than the ones between AU and CH or AU and EU, especially for CaO, Na₂O, MgO and Zn.

The results may indicate differences of the geochemical background, geomorphological and climatic environments in Australia, China and Europe. Elements that easily migrate with water, such as Ca, Mg, Na, and K, are leached and depleted in the weathered materials, leaving insoluble elements like Si, Ti, Al, Fe, and Zr relatively enriched, as noted also by Reimann et al. (2012). Depressed median values for Ca, Mg, Na, K, etc. in Australia show that these elements are significantly more leached than in China and Europe, probably due to protracted weathering. Australia's tectonic stability has caused ancient landscapes to be preserved. This stability and landscape longevity have resulted in a continent that is deeply weathered and soil that is nutritionally poor and fragile. Such sustained weathering results in the formation of abundant Fe oxides in the deep regolith, giving the Australian landscape its distinctive red colour. It should be no surprise that many elements are depleted in Australian soil and floodplain sediment.

The generally higher values, median included, of the CH dataset compared to the other two could partly be explained by the smaller grain size fraction analysed here (<1 mm) compared to AU and EU (<2 mm). Generally the concentration of elements, including trace elements, increases as the analysed grain size fraction becomes finer, with the opposite behaviour for SiO₂ (e.g., Acosta et al., 2011). This is the result of chemical/mineralogical as well as physical changes: the abundance of clay minerals, Fe-oxyhydroxides and other particles containing less Si and having greater surface areas available for the adsorption of elements increases with decreasing grain size fraction.

5. Conclusions

The analytical results of catchment/floodplain sediments in three continental-scale geochemical mapping projects (AU, CH and EU) were compared by considering: sample media, sample preparation, elements determined, analytical methods, detection limits and proportions of reportable values, and certified reference materials used. The main conclusions are:

- (1) Criteria for selecting globally comparable or harmonised datasets from country- or continent-wide geochemical mapping projects were proposed in this paper. These criteria and methods could be used to select comparable datasets from completed national- and continental-scale geochemical mapping projects, though international or exchanged reference standard materials have not been used in their quality control procedures.
- (2) Twenty six elements (Ba, Ce, Co, Cr, Cu, Mo, Nb, Ni, Pb, Rb, Sr, Th, V, Y, Zn, Zr, Al₂O₃, CaO, Fe₂O₃ (total), K₂O, MgO, MnO, Na₂O, P₂O₅,

SiO₂, TiO₂) were demonstrated to be comparable among the 35 elements determined by all three projects (AU, CH and EU).

- (3) The medians of most elements in the three datasets are in the order CH > EU > AU, except Co, Y and TiO₂ (CH > AU > EU), Zr (AU > CH > EU), and SiO₂ (AU > EU > CH). The median CH/EU ratios for all elements range from 0.98 to 1.94, while the median EU/AU and CH/AU ratios for soluble elements such as CaO, Na₂O, MgO, and Zn are greater than 2. Soluble elements appear to be significantly more leached in sediments from Australia than China and Europe, probably due to protracted weathering in Australia. The difference between CH and EU is significantly smaller than the ones between AU and CH or between AU and EU indicating that China and Europe are more alike in climate or geomorphological environments. The finer grain size analysed in CH partly explains the generally higher values (including medians) observed in CH compared to EU.
- (4) Unified sample media are proposed to be collected, and unified sample preparation techniques (e.g., grain size fractions) are proposed to be followed in order to obtain globally comparable datasets for the establishment of global geochemical baselines.
- (5) Chemical analysis is the most crucial problem when comparing datasets obtained from different laboratories. Key elements related to mineral resources and the environment have to be determined and detection limits for all elements must be lower than crustal abundance values, and international or exchanged standard materials must be inserted in any new regional-, national- or global-scale geochemical mapping projects.

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