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China geochemical baselines: Sampling methodology

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ABSTRACT

The China Geochemical Baselines Project (CGB) was launched in 2008, and sampling was completed in 2012. Its purpose is to document the abundance and spatial distribution of chemical elements covering all of China. The database and accompanying element distribution maps represent a geochemical baseline against which future human-induced or natural chemical changes can be quantified. The sampling methodology was updated or developed for China's diverse landscape terrains of mountains, hills, plains, desert, grassland, loess and karst in order to obtain nationwide high-resolution and harmonious baseline data. Floodplain sediment or alluvial soil was used as the sample medium in plain and hilly landscape terrains of exorheic river systems in eastern China. Overbank sediment was adopted as the sampling medium in mountainous terrains of exorheic river systems in south-western China. Methods of collecting catchment basin and lake sediments were developed in desert and semi-desert terrains, respectively, in endorheic drainage systems in northern and north-western China. Two sampling sites were allocated to each CGB grid cell of 1° (long.) \times 40' (lat.), approximately equal to 80 \times 80 km in size. At each site, two samples were taken; one from a depth of 0–25 cm and a second, deeper sample from a depth greater than 100 cm or the deepest part of horizon C as possible as we can take. A total of 6617 samples from 3382 sites have been collected at 1500 CGB grid cells across the whole of China (9.6 million km²), corresponding to a density of approximately one sample site per 3000 km². In addition, 11,943 rock samples have also been collected to aid in the interpretation of geogenic sources of elements. Before chemical analysis, the soil and sediment samples were sieved to <10 mesh (2.0 mm) and ground to <200 mesh (74 µm), rock samples were pulverised to <200 mesh (74 µm). Seventy-six chemical elements plus 5 additional chemical parameters of Fe^{2+} , organic C, CO₂, H_2O^+ and pH were determined under strict laboratory analytical quality control. An Internet-based software named Digital Geochemical Earth was developed for managing the database and maps. Initial results show excellent correlations of element distribution with lithology, mineral resources and mining activities, industry and urban activities, agriculture, and climate.

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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 spatial baseline distribution in the Earth's surface or near-surface environment (Wang et al., 2006). "How do we recognise and understand changes in natural systems if we don't understand the range of baseline levels?" (Zoback, 2001). Recommendations for carrying out global-scale geochemical mapping were published by Darnley et al. (1995). Since then, slow but significant

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progress has been or is being made on global-scale or continental-scale geochemical baselines.

Active stream sediment has been widely used as a sampling medium for regional/national geochemical mapping for the past several decades (Plant et al., 1988). Overbank sediment was initially recommended for regional geochemical mapping by Ottesen et al. (1989). The Working Group on Regional Geochemical Mapping of the Western European Geological Surveys (WEGS), chaired by Prof. Bjorn Bølviken, after considering the results of pilot project studies carried out in different European countries, recommended its use in low density continental-scale geochemical mapping (Bølviken et al., 1990, 1996; Demetriades et al., 1990). Subsequently, Prof. Xuejing Xie initiated floodplain sediment sampling in China as a pilot study to verify its suitability as sampling medium for global geochemical mapping. Floodplain sediment samples were collected, where available, from 529 sites in eastern China based on a grid of 160×160 km cells from 1994 to 1996 (Wang, 2005; Xie and Cheng, 1997, 2001; Xie et al., 2008). The Geochemical Baseline Mapping Programme of the Forum of European Geological Surveys

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	tion: NGSA: National Geochemical Survey of Australia; EGMON: Environmental Geochemical Monitoring Networks; CGB: China Geochemical Ba	ultural and grazing land soil; NASGLP: North American Soil Geochemical Landscapes Project).
Table 1	Sampling media used by global-/continental-scale geochemical baseline projects (Notatic	FOREGS: Forum of European Geological Surveys; GEMAS: Geochemical Mapping of Agricul

Country	Project	Coverage (million km ²)	Sample medium	Sampling site	Sampling density (1 site/thousand km ²)	Sampling depth (cm)		Grain size (mm)	No. of parameters determined
						Top	Deep		
Australia	NGSA (2006–2011)	6.174	Catchment Outlet sediment	1315	5200	0-10	60-80	<2	63
China	Cantat and Cooper, 2011) EGMON (1992–1997) (Yie ef al 1996)	7.0	Floodplain/stream sediment	843	8300	5-25	80-120	$\stackrel{\wedge}{.}$	50
	CGB (2008–2013) (Many 2012)	9.3	Floodplain/overbank/catchment	3382	3000	0-25	>100/C-horizon	<2	81
Europe	FOREGS (1996–2005)	4.25	Humus	006	4700	0–3	/	<2	12
	(Salminen et al., 2005; De Vos et al., 2006)		Water					-	66
			Stream sediment Soil			0-25	50-200	<0.15 <2	54 61
			Floodplain sediment	790	5300	0-25	/	<2	54
	GEMAS (2007–2013)	5.6	Agricultural soil	2211	2500	0-20	/	<2	73
	(Reimann et al., 2009, 2011, 2012, 2014a, b)		Grazing land soil	2118		0-10	/	<2	73
USA	NASGLP (2007-)	10.0	Soil	6184	1600	0-5; A-horizon	C-horizon/100	<2	45
	(Smith, 2009; Smith et al., 2009, 2012a, 2013;								
	Woodruff et al., in this issue)								

(FOREGS, now EuroGeoSurveys) was conducted between 1997 and 2006 (Plant et al., 1996, 1997; Salminen et al., 1998, 2005) culminating with the publication of a two-volume 'Geochemical Atlas of Europe' (Salminen et al., 2005; De Vos et al., 2006). A suite of geochemical samples, including stream water, stream sediment, topsoil, subsoil, floodplain sediment and humus, was collected from each drainage basin by the FOREGS project. Catchment outlet sediment was used as a sampling medium in the recently completed National Geochemical Survey of Australia (Caritat et al., 2008; Caritat, 2009; Caritat and Cooper, 2011). The U.S. Geological Survey, the Geological Survey of Canada, and the Mexican Geological Survey initiated soil sampling for the North American Soil Geochemical Landscapes Project in 2007 (Friske et al., 2013; Smith, 2009; Smith et al., 2009, 2012a, 2013) with work in the conterminous U.S. completed in 2013 (Woodruff et al., in this issue). Progress has also been made in many other countries (EGS, 2008; Govil et al., 2009, in this issue; Lins et al., 2005; Prieto, 2009; Reimann et al., 2009, 2011, 2012, 2014a,b). Table 1 lists the sampling media used by global- to continental-scale geochemical baseline mapping projects. Approximately 22% of the world's land surface has been covered by these global-scale geochemical projects since the implementation of IGCP Project 259 'International Geochemical Mapping' (1988–1992) and IGCP Project 360 'Global Geochemical Baselines' (1993–1997) (Darnley, 1990, 1995, 1997; Darnley and Garrett, 1998; Smith et al., 2012b). Fig. 1 shows the global sampling coverage.

However, critical problems of sampling and laboratory analysis still exist. Firstly, optimal sampling methodologies need to be updated or developed for the world's diverse landscape terrains; secondly, some key elements for environmental studies and mineral resource investigations have not been determined, and although international reference standards are available to control between-laboratory variations, these are not used by continental-scale projects to compare their results. This paper will particularly focus on the sampling methodology used in the diverse terrains of China by the China Geochemical Baselines project.

2. A general overview of the CGB project

2.1. History of China global-scale sampling

In view of recognising the need to establish global-scale geochemical baselines, based on low density sampling of the Earth's surficial materials (Darnley et al., 1995), Prof. Xuejing Xie initiated the Environmental Geochemical Monitoring Networks (EGMON) project in China from 1992 to 1997. This project, as a part of the IGCP 259/360 pilot study, has verified that floodplain sediment is a suitable sampling medium for global-scale geochemical mapping (Cheng et al., 1997; Xie and Cheng, 1997; Xie et al., 1996, 1997). Floodplain sediment samples were taken at 529 sites in low mountainous or hilly terrains and the plains of eastern China, covering approximately 5 000 000 km². An additional 314 stream sediment samples were collected from river beds in the high mountainous regions of Tibet, south-western China, covering approximately 2 000 000 km² (Fig. 2). Samples were not taken in other terrains, such as in desert (including the Gobi desert) and grassland in northern and north-western China where floodplain and stream sediments are not available.

A new project named China Geochemical Baselines Project (CGB Project) was launched in 2008 (Wang, 2012; Wang et al., 2010, 2011). The project is intended to both monitor the original EGMON sites for possible chemical changes and to provide high-resolution and high-quality geochemical baseline data by developing improved sampling protocols and laboratory analysis, which were not available to the EGMON project.

2.2. Objectives and tasks of the CGB project

The primary goal of the CGB project is to provide high-quality geochemical data and element distribution maps of nearly all naturally

es;

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Fig. 1. Global sampling coverage with sample locations of some completed continental-scale projects (green - completed; yellow - not yet completed).

occurring chemical elements in the Earth's surface to meet the growing requirements for geochemical information to aid in the sustainable development of natural resources and in protecting the environment. Sampling is based on the geochemical baseline network covering the whole of China. The resulting database and accompanying element distribution maps represent the current (2009–2012) geochemical baseline against which future human-induced or natural chemical changes can be quantified or recognised.

The tasks of the project are:

- (1) To develop new, or improve existing, sampling methods suitable for China's diverse terrains, particularly for desert (including Gobi) and grassland, where well-researched sampling media, such as floodplain, overbank and stream sediments are not available.
- (2) To design China Geochemical Baselines Network (CGB Network) with 1500 grid cells (longitude 1° by latitude 40′ for each cell) and approximately 3000 sample sites (2 sites within each cell).
- (3) To collect approximately 6000 catchment sediment/alluvial soil samples (3000 top and deep samples, respectively) and simultaneously take representative rock samples within each cell, if exposed rocks are available.
- (4) To develop analytical methods for the determination of 81 geochemical parameters including 76 elements plus 5 chemical parameters (Fe²⁺, organic C, H₂O⁺, CO₂, pH) under strict quality control protocols.
- (5) To manage the database and maps through an Internet-based software, *Digital Geochemical Earth* (copyright), which is developed by funds from this project.
- (6) To identify areas of interest for mineral resources and environmental protection, and to interpret geogenic and humaninduced sources of the geochemical patterns.

2.3. Timeline and organisation of the CGB project

The CGB project, as a part of the Deep Exploration in China (Sinoprobe) (Dong and Li, 2009), was proposed in 2005. A series of

feasibility study meetings and workshops was held in 2005–2007 to develop the design for sample collection and to establish recommendations for sampling protocols, analytical methods, and data management. The project was accepted and launched in 2008. A five-year term from 2008 to 2012 was approved and financially supported by the Chinese government. A one-year pilot study began in 2008 to test and refine the recommended protocols and to optimise field logistics for the geochemical sampling in China's diverse landscape terrains. After completion of the pilot study, sampling of 6617 catchment sediment/alluvial soil and 11 943 rock samples was conducted from 2009 to 2012. Laboratory analysis was completed in 2013. A geochemical atlas is expected to be published in 2014.

The Ministry of Finance of the People's Republic of China provided the funding for this project. The Ministry of Land and Resources is responsible for the project's management. The coordinating organisations are the China Geological Survey and the Chinese Academy of Geological Sciences. The project is executed by the Institute of Geophysical and Geochemical Exploration (IGGE). The project is led by Prof. Wang Xueqiu (IGGE) and Mr. Zhang Qin (IGGE) and supervised by Prof. Xuejing Xie (IGGE). The sampling was conducted by the CGB team from the IGGE in cooperation with the Hebei Regional Geological Survey, the Henan Geological Survey and Shijiazhuang University of Economics. Samples were prepared and 75 geochemical parameters were determined by the IGGE laboratory and PGEs were analysed by the Henan Centre for Rock and Mineral Analysis.

3. Sampling methodology

3.1. General guidelines for sampling

The general guidelines used for the entire sampling campaign in the CGB project are as follows:

1) Two sampling sites are designated within each CGB grid cell of 1° (long.) \times 40′ (lat.), approximately equivalent to 80 by 80 km on the basis of GRN cells established by Darnley et al. (1995). The sample density is 1 site per 3000 km².



Fig. 2. Distribution of sampling sites for EGMON project (532 floodplain sediment and 314 stream sediment sites) (modified from Xie et al., 1997).

- 2) Samples are taken at drainage catchments ranging in area from about 1000 to 5000 km², with most being 2000–3000 km² in area. The sample sites are selected from at least the two large catchments in each grid cell. It is required that the sample sites are distributed as evenly as possible throughout the whole of China.
- 3) Two 25-cm thick samples are collected at each site: a top sample from the A-horizon and a deep sample from the C-horizon. Sampling depth is not constant in different landscape terrains, and soil horizons are never mixed. Top samples are generally collected from the A-horizon at a depth of 0–25 cm or from the surface to the



Fig. 3. Global Reference Network (GRN) grid covering the whole terrestrial surface of the Earth (modified from Darnley et al., 1995).



Fig. 4. China Geochemical Baselines Network grid cells with sample locations.

bottom of the A-horizon if the thickness of A-horizon is less than 25 cm; deep samples are taken from the C-horizon at a depth of more than 100 cm, and if the top of the C-horizon is deeper than

100 cm or from the deepest part of C-horizon as possible, or from the C-horizon if the soil profile does not have a thickness of more than 100 cm.



Fig. 5. China geomorphological landscape terrains.

Fig. 6. An external or exorheic drainage system showing relationship of overbank and floodplain sediments.

- 4) Samples are composited from generally 3 pits in a layout of an equilateral triangle within 50 m interval. The weight of each sample is about 5 kg.
- The number of duplicate samples exceeds 3% of the total number of samples.
- 6) Samples are not collected within 100 m of motorways/highways or roads, or within 2000 m of towns or cities.

3.2. Design of the CGB network

Approximately 400 Global Reference Network (GRN) grid cells (160×160 km) (Darnley et al., 1995) cover the whole China mainland (Fig. 3). The CGB Project is designed to divide each GRN grid cell into 4 quadrants or CGB grid cells (80 by 80 km), totalling approximately 1500 CGB grid cells covering the whole China mainland (9.6 million km²). The area of each CGB grid cell is approximately equivalent to that of a 1:200 000-scale map sheet of 1° (long.) × 40′ (lat.) in China. In practice, a map sheet of 1:200 000 is used as the CGB grid cell to collect samples (Fig. 4). This design allows for data interpretation and rock sampling by using geological maps at a scale of 1:200 000, which are available throughout China. Generally, two sampling sites within each CGB grid cell are designated, resulting in approximately 3000 sites across the whole of China.

3.3. Geomorphological landscapes and drainage systems in China

The territory of China lies between latitudes 18° and 54° N, and longitudes 73° and 135° E. China's landscapes vary significantly across its vast width as shown in Fig. 5. In the east and north-east, there are hilly or low mountainous areas, alluvial plains, and forested land. Northern and north-western China is dominated by arid desert basins (including the Gobi desert), semi-desert grassland and loess plateaus. High mountains prevail in south-western China, most notably the Himalayas. The project had to improve existing methods or develop new methods of sampling in these diverse terrains in order to establish harmonised, national-scale, high-resolution data.

It is necessary to have a good understanding of the drainage systems if samples are to be collected on the basis of drainage catchments. In China, drainage systems are classified into two types: external or exorheic and internal or endorheic drainage systems (Neuendorf et al., 2011; http://en.wikipedia.org/wiki/Endorheic_basin). Fig. 5 shows the geomorphological landscape terrains in China; eastern, north-eastern and south-western China, including hilly terrains (A area), alluvial plains (B area), forests (C area), karst terrain (D area) and high mountainous terrains (F area), belong to the exorheic river system; northern and north-western China are dominated by the endorheic basin systems including Gobi desert (I area), desert basin (J area), grassland terrains (H area) and cold swampy terrains (G area).

Floodplain and overbank sediments are generally formed in an exorheic drainage system where water constantly flows out to the ocean under a relatively wet climate (Fig. 6). Floodplain sediments were proven as an effective medium in relatively open terrains (hilly and flat terrains) in eastern China (Fig. 5, A and B area) (Xie et al., 1997). Overbank sediment was initially recommended as a sampling medium by Ottesen et al. (1989) and Bølviken et al. (1990, 1993, 1996), and subsequently proven as an effective medium available in mountainous, hilly and island terrains (Cheng et al., 1997; Demetriades et al., 1990; Wang, 2005; Xie and Cheng, 1997, 2001; Xie et al., 2008). Overbank and floodplain sediments are both alluvial materials deposited by floodwater. The term overbank sediment is used for alluvium accumulated adjacent to low-order streams, and floodplain sediment to alluvium adjoining high-order drainage channels, typically large rivers (Darnley et al., 1995). The former are dominant in mountainous terrains, and the latter in plain terrains. Fig. 6 shows the relationship of overbank and floodplain sediments. Overbank and floodplain sediments are the first choice for global-scale sampling media for exorheic drainage system terrains in China, because of their excellent homogeneity and geochemical representativeness of the catchment basin (Bølviken et al., 1990,

Fig. 7. An endorheic basin system in desert and semi-desert inland terrains.

Fig. 8. Picture showing endorheic basin sediments in desert and semi-desert inland terrains.

1996; Cheng et al., 1997; Demetriades et al., 1990; Ottesen et al., 1989; Xie and Cheng, 1997).

There is little research on global-scale sampling for internal or endorheic drainage systems in arid and semi-arid inland terrains. Arid or semi-arid Gobi and desert terrains occupy approximately one third of the Earth's land surface and cover an area of approximately 2.2 million km² in China (Fig. 5, G, H, I and J areas). An internal or endorheic drainage system is also referred to as an internal or endorheic basin, which is a closed drainage basin that retains water and allows no outflow to other external bodies of water, such as rivers or oceans (http://en.wikipedia. org/wiki/Endorheic_basin). Surface water of endorheic basins deposits sediments at inland terminal locations where the water evaporates or seeps into the ground (Fig. 7). Such drainages may be completely dry during dry seasons (Fig. 8). The basin sediment is a suitable medium for global-scale sampling in desert and semi-desert terrains of China due to the excellent representativeness and homogeneity of transported materials.

3.4. Sample media used in different landscape terrains

Table 2 lists the sample media used and number of sampling sites in different landscape terrains. The sample media are categorised into 4 main types to be described according to the primary landscape terrains in China, including (1) hilly and alluvial plain terrains; (2) high mountainous and cold swampy terrains; (3) desert terrains; and (4) grassland terrains (Fig. 5).

3.4.1. Floodplain sediment/alluvial soil in hilly and alluvial plain terrains in eastern China

In hilly and alluvial plain terrains of eastern China (Fig. 5, A, B and C areas), floodplain sediments are deposited at a catchment outlet flat area during flood events in low energy environments (Mariott and Alexander, 1999; Ottesen et al., 1989). Two sampling locations were designated in the two largest catchments, which are representative of over 80% of each CGB grid cell, such as cells A₁, A₂, A₃, A₄ (Fig. 9). Samples are taken at the mouth of a drainage catchment, which generally controls an area of 1000-3000 km². The sampling location is generally selected at a distance of over 10 m away from the river bank (Fig. 9). In flat agricultural land, alluvial soil is, thus, also the optimum sample medium. For grids B₁ and B₃ (Fig. 9), one catchment sediment sample was taken from a catchment and one alluvial soil sample at plain areas. For B₂ and B₄ (Fig. 9) two alluvial soil samples were collected at flat areas. Top samples are collected from 0 to 25 cm, and 25-cm thick deep samples under a depth of 100 cm by using a special sampling tool (Fig. 10). Samples are composited from generally 3 pits within 50 m intervals, and are always collected from single layers. Care is also taken to collect the composite sample from the same floodplain sediment horizon; hence, the 25-cm thick sampling interval may be less in some cases.

3.4.2. Overbank sediment in mountainous terrains

Overbank sediments are widely available in mountainous terrains (Fig. 5, F area). Their characteristics are similar to that of floodplain

Table 2

Number of sampling locations of the CGB project in geomorphological landscape terrains.

Terrain type	Sample medium	Area (km ²)	Number of sampling sites
Hills (Fig. 5, A)	Floodplain sediment	1,571,095	633
Alluvial plains (Fig. 5, B)	Floodplain sediment or transported soil	874,172	335
Swampy and forestry terrains (Fig. 5, C)	Floodplain sediment	613,759	218
Karst (Fig. 5, D)	Floodplain or overbank sediment	365,670	126
Loess (Fig. 5, E)	Floodplain or overbank sediment	411,033	170
High mountains (Fig. 5, F)	Overbank sediment	2,761,597	923
Cold swampy (Fig. 5, G)	Floodplain or lake sediment	725,499	140
Semi-desert grassland	Lake or catchment basin sediment	421,892	215
(Fig. 5, H)			
Gobi desert (Fig. 5, I)	Catchment basin sediment	769,243	424
Basin desert (Fig. 5, J)	Catchment basin sediment	719,148	198
Total		9,233,107	3382

Fig. 9. Sampling layout of floodplain sediments at catchment basins and flat plain areas.

sediments. The difference is that overbank sediments are restricted to a mountain valley, whereas floodplain sediments are deposited in an open plain area (Darnley et al., 1995). Samples of overbank sediments are taken at the mouth of a catchment draining an area of 1000–3000 km². Two samples are collected from the largest two catchments covering over 80% of a grid cell. The sampling location is generally selected at a distance of 10 m away from the river bank. Top samples are collected from 0 to 25 cm, and 25-cm thick deep samples under a depth of 100 cm by using a special sampling tool (Fig. 11) or by using a natural profile if the river valley is so narrow that overbank sediments do not extend a distance of several metres away from the river bank. Samples are composited from generally 3 pits within 50 m intervals, and are always taken from single layers. Care is also taken to collect the composite sample from the same overbank sediment horizon; hence, the 25-cm thick sampling interval may be less in some cases.

3.4.3. Catchment basin sediment in desert or Gobi terrains

A desert is a landscape or region that receives an extremely low amount of precipitation, less than enough to support the growth of most plants. Deserts are defined as areas with an average annual precipitation of less than 250 mm per year or as areas where more water is lost by evapotranspiration than falls as precipitation (http:// en.wikipedia.org/wiki/Desert). In general, there are five desert forms: 1) Mountain deserts; 2) Basin deserts; 3) Hamada deserts, which consist of plateau landforms; 4) Gobi, which consists of rock pavements; and 5) ergs, which are formed by sand seas (Philips and Comus, 2000). Problems exist when applying the conventional geochemical sampling procedures in desert terrains. Since desert terrains make up approximately one third of the Earth's land surface, it is necessary to develop global-scale sampling methods suitable for this specific type of terrain.

Basin desert (Fig. 5, J area) and Gobi desert (Fig. 5, I area) terrains are widely distributed in the north and north-west of China, covering an area of approximately 2.2 million km².

In basin desert terrains, some desert soil, except ergs, looks like a layer cake with one or more clayey horizons directly above the white calcic horizon. These clay-rich layers are called argillic horizons (Fig. 12) formed over a long period of time when clay particles suspended in water are carried downward into the soil and accumulate. In some parts of the desert, argillic horizons may contain locally more than fifty per cent clay. Periods of abundant rainfall can convert these clay-rich layers into sticky traps that a vehicle can easily be mired down. In

Fig. 10. Floodplain sediment sampling.

Fig. 11. Overbank sediment sampling.

contrast, during the dry season, these clay-rich horizons become as hard as adobe brick. When they are dry, strongly developed argillic horizons often have a pronounced prismatic or blocky structure that is a product of repeated swelling and shrinking of the clay. The presence of calcium carbonate apparently causes clay particles to coagulate together in a way that prevents them from being dispersed in water, thereby inhibiting the downward movement and accumulation of the clay into argillic horizons.

In desert terrains, internal catchment basins are widely distributed. Clay- and silt-sized sediments are deposited in the catchment basin by seasonal rainfall (Fig. 8). The clay-rich horizon is an excellent sampling medium for geochemical mapping, both for environmental and mineral resource purposes. The clay-rich soil is the natural "trap" for accumulating chemical elements and compounds, which are dispersed from sources such as mineral deposits and human pollution. Two samples were collected at the lowest location of the two largest basins ranging from 1000 to 3000 km² for each CGB grid cell (Fig. 13). Surface samples are taken from the clay-rich horizon usually from a depth of 0–10 cm, and deep samples are collected under a depth of 40 cm or at the greatest depth possible. Composite samples are taken from 3 sub-sites within a radius of 50 m. Care is taken to collect composite samples from the same horizon.

In Gobi desert terrains, if the layer of stones from a pavement surface is carefully removed, a distinct, fine-grained soil horizon called a vesicular A (or Av) horizon is often found. The Av horizon is also called desert crust as the topmost layer of soil is formed by cementing together fine dust particles (Fig. 14). The name 'vesicular' refers to the many vesicles or large pores found throughout the horizon (Philips and Comus, 2000). The Av horizon is typically a few centimetres thick, and contains mostly silt and clay; it lacks coarse-grained materials, even though small stones of the pavement cover the Av horizon and rocky materials occur in the soil underlying it.

The origin of the fine-grained Av horizon (Philips and Comus, 2000) is an important key to understanding how the overlying flat-topped pavement develops. The materials in this horizon did not originate from the weathering of the rocky parent materials. Instead, dust deposited on the stony surface is the source of the silt and clay of the Av horizon (Philips and Comus, 2000). These fine-grained materials accumulate beneath a layer of surface stones, separating these stones from the rest of the underlying rocky materials. Over time, the further accumulation of fine-textured materials in the Av horizon literally lifts the mono-layer of stones of the pavement and levels the surface.

Once the desert crust is broken, an abundance of dust can be released into the air by the wind or other disturbances. Humans are then exposed to these microscopic particles that, when inhaled, can potentially be harmful. Some individuals are more sensitive to the effects of dust and can experience major health problems, including asthma and bronchitis.

Fig. 12. Desert catchment basin terrain with a cross-section view of a piece of fine-textured argillic horizon showing the air-filled vesicles.

Fig. 13. A diagram showing sediments deposited at the catchment basin by seasonal rainfall.

The desert crust within a catchment basin is also an excellent sampling medium for global geochemical mapping, particularly for environmental purposes. The samples were collected at the lowest places of the two catchment basins (Fig. 15) generally ranging from 1000 to 3000 km². The top samples are taken from the desert crust by removing the pavement pebbles. The crust is easily recognised as the topmost layer of soil with air-filled vesicles (Fig. 14). The deep samples are taken under a depth of 40 cm or the deepest part accessible. Composite samples are taken from 3 sub-sites within a radius of 50 m. Care is taken to collect composite samples from the same horizon.

3.4.0.4. Lake sediment in semi-desert grassland terrains. In semi-desert grassland, catchment basins or lakes are widely distributed though there are no rivers (Fig. 16). Alluvial sediments are deposited in the lakes by seasonal rainfall, but the lakes may completely dry up during dry season. The lakes with clay and silt sediments make them excellent sampling sites for global-scale geochemical mapping. The mud samples are taken from the exposed lake bottom (Fig. 16). Top samples are collected from a depth of 0–20 cm and deep samples from a depth under 100 cm or the deepest accessible depth.

Rock samples are simultaneously collected in the CGB project. The rock sample data can be used to (1) interpret the geogenic sources of secondary geochemical patterns; and (2) explore the temporal evolution of elements with geological time from Archaeozoic to Quaternary. Typical samples representing the main types of rocks including sedimentary, igneous and metamorphic rocks for different geological times (Precambrian, Cambrian, Ordovician, Silurian, Devonian, Carboniferous, Permian, Triassic, Jurassic, Cretaceous, Tertiary and Quaternary) have been collected in each CGB grid cell. A total of 11 943 rock samples have been collected in 1000 CGB grid cells where exposed bedrock is available (approximately 10 rock samples in each grid cell).

4. Sample preparation, chemical analysis and quality control

4.1. Sample preparation and chemical analysis

Alluvial soil and sediment samples are prepared before sending to the laboratory for analysis. After being air-dried and homogenised, each raw sample of 5000 g is split into two sub-samples, one of 2000 g by sieving to less than 10 mesh (<2 mm) for laboratory analysis and the other of 3000 g for storage and future investigation. A 1000-g sieved

Fig. 14. Gobi desert terrain with a vertical profile and pictorial explanation.

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Fig. 15. Catchment basin sediment sampling in Gobi desert type terrain.

Fig. 16. Lake sediment sampling in semi-desert grassland terrains.

sample is ground to less than 200 mesh (<74 μ m) in an agate mill. A 500-g ground sample is sent to the laboratory for analysis; the other 500 g is placed in a polypropylene bottle and stored in the sample archive room (Fig. 17). Eighty-one geochemical parameters (76 chemical elements of Ag, As, Au, B, Ba, Be, Bi, Br, Cd, Cl, Co, Cr, Cs, Cu, F, Ga, Ge, Hf, Hg, I, In, Ir, Li, Mn, Mo, N, Nb, Ni, Os, P, Pb, Pd, Pt, Rb, Re, Rh, Ru, S, Sb, Sc, Se, Sn, Sr, Ta, Te, Th, Ti, Tl, U, V, W, Zn, Zr, Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, SiO₂, Al₂O₃, Total Fe₂O₃, MgO, CaO, Na₂O, K₂O,) are determined by ICP-MS/AES following 4-acid digestion and XRF on fusion beads as backbone methods combined with 10 other methods, including methods for determining C, Fe²⁺, organic C, CO₂, H₂O⁺ and pH.

All laboratory methods are described by Zhang Qin in Chinese (Zhang et al., 2012) and will be published in English in a future special issue of the CGB project.

4.2. Quality control

The quality control (QC) procedures used accepted methods, and include field training, field sampling checking, field duplicates, detection limits, analytical reportable rate, laboratory replicates and standard reference materials. The QC protocol is briefly described below.

Fig. 17. China Geochemical Baselines sample archive.

Table 3	
Equations and cutoff values for accuracy a	nd precision control.

	Accuracy control by standards	Precision control by standards	Precision co laboratory r	ontrol by replicates	Sampling e by field du	error control plicates	
Equations	$\Delta lgC = lgCi - lgCs $	$RSD = \sqrt{\frac{\sum\limits_{i=1}^{n} (Ci - Cj)^2}{\frac{n-1}{C_i}}} \times 100\%$	RD% = C1 [(C1 + C2)]	. – C2 / /2] * 100%	RE% = Sc [(So + Sd)]	RE% = So - Sd / [(So + Sd)/2] * 100%	
Range of concentrations	Cutoff value	Cutoff value	Cutoff value		Cutoff value		
0			Others	Au, PGEs	Others	Au, PGEs	
Less than 3 times the detection limit	≤0.15	≤17%	≤50%	≤100%	≤50%	≤100%	
Higher than 3 times the detection limit	≤0.10	≤10%	$\leq 40\%$	≤50%		≤50%	
1–5%	≤0.07	≤8%					
>5%	≤0.05	≤3%					

Notation: Ci — the i determination value for the standard; Cs — standard reference value; Cj — average determination value of standards; C1 — the 1st determination value for the laboratory replicate sample; C2 — the 2nd determination value for the laboratory replicate sample; S0 — the determination value for the original field sample; Sd — the determination value for the field duplicate sample.

Sampling quality control began with the preparation of a sampling field manual, which was refined after the one-year orientation. Training in the office and field of all field team members was given before the start of CGB project to ensure all participants were familiar with the field sampling methods. Each sampling team checked 100% of the daily collected samples, including the field observations record card descriptions, the sample quantity, weight, and numbering of the sample, and that the GPS coordinates agreed with the extracted topographic map coordinates. The sampling team leader signed the field observations record cards after the daily check. The project group leader subsequently randomly selected over 5% of the total number of sampling sites and went to the selected field sites to check if the field on-site observations and descriptions agreed with each other, including filed observation records, sampling sites, topographic map and GPS track record, sample media, grain size and weight, and geology if outcropping rocks are available. The project leader or supervisor was obliged to write a sampling quality report and sign it.

Field duplicate samples were taken to control field sampling errors for each sample type. One field duplicate site was designed in every 30 sampling sites to control field sampling errors. A total of 211 field duplicate samples (109 top and 113 deep samples) from 113 control sites were collected out of a total of 3382 sampling sites (6617 samples in total). The relative sampling error (RE%) was calculated based on the absolute difference between pairs (original (So) and duplicate (Sd) samples) divided by the average value of the pairs ((So + Sd)/2), i.e.,

(RE% = |So-Sd|/[(So + Sd)/2] * 100%)

(Table 3) after laboratory analysis. The cutoff value for acceptance of the RE is 50% for all elements except for Au and PGEs which are 100% for concentrations less than 3 times the detection limit and 50% for concentrations higher than 3 times the detection limit, respectively (Table 3). The passing rates are over 90% for most elements except for C Cl, Hg, N and CO₂ (Table 4).

Laboratory analytical quality control began with selection of laboratories and analytical methods. The IGGE Laboratory and Henan Geoanalysis Laboratory, which are the best two laboratories for geochemical analysis in China, were selected to carry out the chemical analysis of the collected samples. The analytical methods used must meet requirements for detection limits below the crustal abundance of elements. Proportion of values over detection limits also called 'reportable rate' has to exceed 90% of the total number of analysed samples. The statistics show that reportable rates are over 90% for all elements except for Br, I, MnO and organic C (Table 4).

Analytical accuracy and precision for the laboratory quality was strictly controlled by laboratory replicate samples and Standard Reference Materials (SRMs). Five laboratory replicates were inserted into each batch of 50 samples for precision control. In total, 660 laboratory replicates were inserted into 6617 samples. The Relative Deviation (RD%) of determination values of the replicates were calculated based on the equation:

$$RD\% = |C1\text{-}C2|/[(C1+C2)/2]*100\% (Table \ 3)$$

where

- C1 is the 1st determination value for the laboratory replicate sample,
- C2 is the 2nd determination value for the laboratory replicate sample.

The requirement cutoff values are 50% for concentrations less than 3 times the detection limit and 40% for concentrations higher than 3 times the detection limit for each elements except for Au and PGEs which are 100% for concentrations less than 3 times the detection limit and 50% for concentrations higher than 3 times the detection limit, respectively (Table 3). The passing rates are 100% for nearly all elements (Table 4). The Standard Reference Materials (SRMs) used in the CGB project include soil standards (GSS-1, GSS-2, GSS-17, GSS-19, GSS-25, GSS-26, GSS-27) (Xie et al., 1985a,b, http://www.gbw114.org/d_120453.htm; http://www.gbw114.org/d_120461.htm), gold standards (GAu2a, GAu2b, GAu9a, GAu9b, GAu10a, GAu10b, GAu11a, GAu11b and platinum group element standards (GPt-1, GPt-2, GPt-7 and GPt-8) (Gu et al., 2001, 2006; Yan and Wang, 1986; Yan et al., 1995, 1998). Four standards were inserted into each batch of 50 samples for accuracy and precision control. In total, 628 standards were inserted into the suite of 6617 samples. Accuracy was controlled by the logarithmic difference (\triangle lgC) of the determination value (lgCi) and standard reference value (lgCs) for each standard, and cutoff values for different concentrations are listed in Table 3. Precision was controlled by the Relative Standard Deviation (RSD) (Table 3). The passing rate for all SRMS is 100% according to the cutoff values for precision (Table 4).

5. Conclusions

The refined field methods used in the CGB project proved to be quite effective in the establishment of nation-wide harmonious geochemical baselines and in the delineation of geochemical anomalies caused by either geogenic or anthropogenic sources. The large amount of data generated by this project required the development of suitable software tools for their management. Hence, an Internet-based software named *Digital Geochemical Earth* was developed for managing the database and map plotting (Nie et al., 2012). The first interpretation of the resulting data and spatial determinant distribution maps indicate that 1) most of the trace elements are more concentrated in the top, near-

Table	4
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Proportion of reportable values, the passing percentage rate of standard reference materials (SRMs), laboratory replicate and field duplicate samples for the CGB project.

Parameters	Sample preparation	Analytical method	Unit	Detection	Reportable	Passing	rates (%)	
				Limit	rate (%)	SRMs	Laboratory replicates	Field duplicate
	Agua ragia	CE/Elamo AAS	ug/kg	0.2	00.4	100	062	01.6
Aα	DC Arc	GI/Hame-AAS	µg/Kg µg/kg	20	99.4	00 2	90.2	91.0
As	Aqua regia	HG-AFS	mg/kg	1	99.7	99.8	98.5	94.9
B	DC Arc	ES	mg/kg	2	100	99.7	98.2	94.9
Ba	Powder pellets	XRF	mg/kg	5	100	100	100	99.5
Ве	4-acid digestion	ICP-OES	mg/kg	0.2	100	100	100	99.5
Bi	4-acid digestion	ICP-MS	mg/kg	0.05	99.8	100	99.5	96.7
Br	Powder pellet	XRF	mg/kg	1.5	65.2	95.8	90.9	90.2
Cd	4-acid digestion	ICP-MS	mg/kg	20	99.9	99.7	100	95.3
С	Powder oxidative combustion	GC	%	0.1	99.6	99.5	96.2	89.3
Cl	Powder pellet	XRF	mg/kg	20	99.2	99.7	95.3	86.0
Co	4-acid digestion	ICP-MS	mg/kg	1	99.9	100	100	99.1
Cr	Powder pellet	XRF	mg/kg	5	99.8	99.7	98.6	95.8
Cs	4-acid digestion	ICP-MS	mg/kg	1	99.8	100	100	99.1
Cu	4-acid digestion	ICP-MS	mg/kg	1	100	100	100	98.1
F	Alkaline fusion	ISE	mg/kg	100	99.6	100	98.5	98.1
Ga	Powder pellet	XKF	mg/kg	2	100	100	100	100
Ge	Actu digestion	HG-AFS	nig/kg	0.1	100	100	99.4	99.1
ПI Ца		CV AES	mg/kg	0.2	100	00.0	96.0	90.1
I	Alkaline fusion	COL	mg/kg	2	877	99.0	90.2	00.0 01 1
In	A-acid digestion	ICP-MS	mg/kg	0.02	93.8	99.0	100	98.1
li	4-acid digestion	ICP-OFS	mg/kg	1	100	100	100	98.6
Mn	Powder nellet	XRF	mg/kg	10	100	100	100	97.7
Mo	4-acid digestion	ICP-MS	mg/kg	0.2	99.2	100	100	97.7
N	Powder oxidative combustion	GC	mg/kg	20	99.9	100	94.6	86.9
Nb	4-acid digestion	ICP-MS	mg/kg	2	100	100	100	98.6
Ni	4-acid digestion	ICP-MS	mg/kg	2	99.9	100	100	97.7
Р	Powder pellet	XRF	mg/kg	10	100	100	100	98.1
Pb	4-acid digestion	ICP-MS	mg/kg	2	100	100	100	99.5
Rb	Powder pellet	XRF	mg/kg	5	100	100	100	99.1
S	Powder pellet	XRF	mg/kg	50	97.8	100	94.4	93.0
Sb	Aqua regia	HG-AFS	mg/kg	0.05	100	100	99.5	98.1
Sc	4-acid digestion	ICP-MS	mg/kg	1	99.9	100	100	99.1
Se	Acid digestion ²	HG-AFS	mg/kg	0.01	100	100	98.9	96.7
Sn	DC Arc	ES	mg/kg	1	98.7	98.9	97.6	95.3
Sr	4-acid digestion	ICP-OES	mg/kg	5	99.8	100	100	98.1
la Te	4-acid digestion	ICP-MS	mg/kg	0.1	100	99.7	99.1	97.7
ть	4-acid digestion	ICP-IVIS	nig/kg	0.01	99.9	98.1	98.8	99.1
Ti	4-actu digestion Powder pollet	VPE	mg/kg	10	100	100	100	96.0
T1	A-acid digestion		mg/kg	0.1	100	100	100	99.1
II	4-acid digestion	ICP-MS	mg/kg	0.1	100	100	100	98.0
v	Powder nellet	XRF	mg/kg	5	100	100	100	99.1
Ŵ	4-acid digestion	ICP-MS	mg/kg	0.2	100	100	99.4	98.6
Zn	4-acid digestion	ICP-MS	mg/kg	2	100	100	100	98.1
Zr	Powder pellet	XRF	mg/kg	2	100	100	99.4	98.1
Ce	4-acid digestion	ICP-MS	mg/kg	1	100	100	100	99.1
Dy	4-acid digestion	ICP-MS	mg/kg	0.1	100	100	100	98.1
Er	4-acid digestion	ICP-MS	mg/kg	0.1	100	100	100	98.1
Eu	4-acid digestion	ICP-MS	mg/kg	0.1	100	100	100	99.5
Gd	4-acid digestion	ICP-MS	mg/kg	0.1	100	100	100	98.1
Но	4-acid digestion	ICP-MS	mg/kg	0.1	100	100	100	98.6
La	4-acid digestion	ICP-MS	mg/kg	1	100	100	100	99.1
Lu	4-acid digestion	ICP-MS	mg/kg	0.1	99.8	100	100	98.6
Nd	4-acid digestion	ICP-MS	mg/kg	0.1	100	100	100	99.1
Pr	4-acid digestion	ICP-MS	mg/kg	0.1	100	100	100	99.1
SM	4-acid digestion	ICP-IMS	mg/kg	0.1	100	100	100	99.1
I D Tree	4-acid digestion	ICP-IMS	mg/kg	0.1	100	100	100	98.6
1111 V	4-acid digestion	ICP-IVIS	nig/kg	0.1	99.8	100	100	98.0
I Vb	4-acid digestion	ICP-IVIS	mg/kg	1	100	100	100	96.1
Pt	Nis-Fire Assav	ICP-MS	mg/kg	0.1	99.9	100	946	100
Pd	Nis-Fire Assav	ICP-MS	mo/ko	0.05	99.4	100	948	100
Ir	NiS-Fire Assav	ICP-MS	mg/kg	0.01	98.7	100	93.7	96.7
Rh	NiS-Fire Assav	ICP-MS	mg/kg	0.01	97.5	100	92.0	99.5
Os	Alkaline fusion	COL	mg/kg	0.01	98.9	100	91.7	98.6
Ru	Alkaline fusion	COL	mg/kg	0.01	99.8	100	92.6	99.5
SiO ₂	Fused pellet	XRF	%	0.1	100	100	100	100
Al ₂ O ₃	Fused pellet	XRF	%	0.1	100	100	100	100
Fe ₂ O ₃	•	Calculation	%	0.1	99.9	100	100	98.1
FeO	Acid digestion ³	VOL	%	0.1	99.7	100	98.9	93.5
MgO	4-acid digestion	ICP-OES	%	0.05	100	100	100	99.1

(continued on next page)

Parameters	Sample preparation	Analytical method	Unit	Detection	Reportable	Passing	rates (%)	
				Limit	rate (%)	SRMs	Laboratory replicates	Field duplicate
CaO	Fused pellet	XRF	%	0.05	99.9	100	100	98.1
Na ₂ O	4-acid digestion	ICP-OES	%	0.05	99.7	100	100	99.1
K ₂ O	Fused pellet	XRF	%	0.05	100	100	100	100
MnO	Fused pellet	XRF	%	0.05	79.1	100	100	98.1
P_2O_5	Fused pellet	XRF	%	0.05	95.9	100	100	98.1
TiO ₂	Fused pellet	XRF	%	0.05	100	100	100	99.1
H_2O^+		Gravimetry	%	0.1	100	100	98.6	98.1
CO ₂		Calculation	%	0.1	95.6	100	83.9	64.5
Total Fe ₂ O ₃	Powder pellet	XRF	%	0.1	100	100	100	99.1
Org. C	Powder oxidative combustion	Potentiometry	%	0.1	88.9	97.0	94.4	88.8
рН	1:2.5 (soil:water)	Potentiometry	0.1 (Sensitivity)	-	100	98.8	100	pН

Notation: 4-acid digestion: HF, HNO₃, HClO₄, aqua regia; ¹acid digestion: HF, HNO₃, H₂SO₄; ²acid digestion: HF, HNO₃, HClO₄, HCl; ³acid digestion: HF, H₂SO₄; COL: Colorimetry; CV-AFS: Cold Vapour Atomic Fluorescence Spectroscopy; ES: Emission Spectrometry; GF/Flame-AAS: Graphite furnace/Flame Atomic Absorption Spectrometry; HG-AFS: Atomic Fluorescence Spectrometry; ICP-MS: Inductively Coupled Plasma Mass Spectrometry; ICP-OES: Inductively Coupled Plasma Optical Emission Spectrometry; ISE: Ion Selective Electrode; XRF: X-Ray Fluorescence Spectrometry; SRM: Standard Reference Material; Laboratory replicates: laboratory replicate analysis; Field duplicates: field duplicate samples

surface, sample than in the deeper sample; 2) the concentration of many potentially toxic elements, such as Cd, Hg, As, Pb, P and the halogens, in surface soil are influenced by human activities; 3) some metals associated with mineralisation, such as W, Sn, Au, Ag, Cu, REE are correlated with metallogenic provinces; 4) some elements, such as Ti, V, Co, Ni, Cr, Fe, Mn and PGEs, are correlated with lithology, particularly related to mafic or ultramafic rocks such as basalts; and 5) some major elements, such Ca and Al, show the influence of both climate and geology. The CGB project results will be described fully in the pending geochemical atlas and subsequent papers.

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