



What controls selenium release during shale weathering?

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ABSTRACT

This study demonstrates that only a combination of a chromous chloride reduction with dual sequential extraction schemes can clearly separate the proportions of Se present in the sulphide versus the organic pools in shales. The data reveals that even small amounts of pyrite outcompete the organic matter for the available Se and pyrite oxidation will control the release of selenium during shale weathering.

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1. Introduction

The prime natural source of Se is carbonaceous shales, which can contain bulk Se concentrations up to 9.1% (Yang and Xia, 1995). Shales are naturally heterogeneous and usually consist of three main host phases: sulfides, silicates and organic matter. Selenium can be present in all these host phases as inorganic Se in up to four oxidation states and also as organic Se compounds. These hosts all have varying solubilities, reactivities and thus bioavailabilities. Weathering usually transforms most inorganic Se into more oxidized and thus much more toxic species (Zawislanski et al., 2003). Crucially, the weathering driven release and Se speciation is dependent on its chemical form and bonding in the host phase, but these processes are currently poorly understood. The lack of a quantitative understanding of the occurrence and distribution of Se in each host phase, therefore, assessment of the release and associated speciation change during weathering, and consequently limits understanding of sources of Se into natural waters. The current study directly quantifies the occurrence and distribution of Se in shale host phases via sequential extractions with the goal to predict the Se release patterns during weathering.

2. Methods

Shale samples from the UK (West Yorkshire; $n = 5$), Colombia (Villeta, $n = 1$), and China (Yutangba; $n = 4$) were pulverized and sieved to below 100 mesh (0.152 mm). Organic C (C%) and inorganic S (S%) contents were quantified via elemental analysis (EA-IRMS; Eurovector EA3000-GV Isoprime). The mineralogical composition was determined via X-ray diffraction (XRD, Phillips PW1050 diffractometer, Cu K α radiation) with the relative percentages of phases derived by Rietveld refinement (Topas; v.4.2).

Two sequential extraction protocols were applied (Fig. 1) in order to differentiate between the various Se environments:

- *Protocol A*, follows a six-fraction scheme modified after Kulp and Pratt (2004) but combining their last two fractions into one residual fraction (Fig. 1A).
- *Protocol B*, Lussier et al. (2003) with a four-fraction scheme (Fig. 1B).

In addition, using a separate one-step reduction (Newton et al., 1995) with Cr(II)Cl₂ the Se contents in diselenide minerals and Se substituted for S in pyrite were quantified. This reduction also releases Se (IV) and Se(0) but not Se bound to organic matter (Velinsky and Cutter, 1990).

All extracted solutions were analyzed for Se with a high-resolution continuum source atomic absorption spectrometer (AAS, ContrAA[®] 700, Analytik Jena) using the HydrEA technique. This approach combines graphite furnace AAS with classic hydride generation (Agterdenbos and Bax, 1986).

3. Results and discussion

3.1. Bulk selenium, organic carbon and inorganic sulfur

The UK (S1–S5) and Colombian (S7) sample set represent common sedimentary shales with bulk Se concentrations between 0.80 and 10.00 $\mu\text{g/g}$ (Table 1). In contrast, the Chinese (S8–S11) samples (although also shales) have atypically high, bulk Se concentrations (160–5300 $\mu\text{g/g}$). There are distinct differences between these two sets of samples including inorganic S (S%, pyrite) and organic C (C%) contents (Table 1) with the UK/Colombian set having average S% between 0.50% and 2.75% and moderate to high levels of C% (1.9–6.6). On the other hand, the Chinese samples contain very low concentrations of inorganic S (<0.06%) but extremely high organic C contents (~10–30%). The XRD quantification (Table 1) also revealed that the UK/Colombia samples are composed of phyllosilicates (~30–70%) with smaller percentages of aluminosilicates (~11–25%), quartz (4–20%) and pyrite (0.2–5.1%). However, almost all the Chinese samples contain high percentages of quartz (~70–

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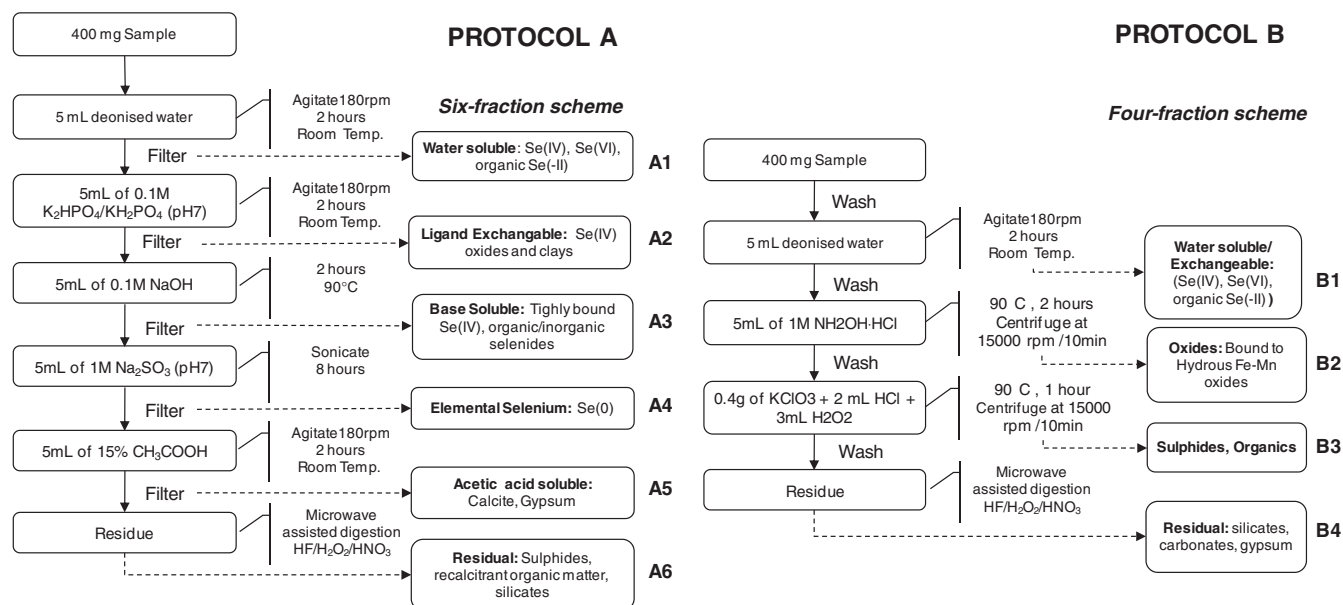


Fig. 1. Sequential extraction protocols with the various fractions in bold.

80%), only low concentrations of all other silicates and no pyrite, confirming the low inorganic S content.

3.2. Occurrence and distribution of selenium in shales

Overall, for all samples, the comparison and correlations between the results from the two protocols are in a good agreement (Table 2) and the distribution of Se among the different fractions is graphically shown in Fig. 2.

In all samples and in both sequential protocols, the Se concentrations in the *water soluble* and the *ligand exchangeable* fractions (e.g., fractions A1 and A2 in Fig. 1, Protocol A) were $\leq 10\%$ of total Se.

The most prominent observation from Fig. 2 is that overall, Se was associated with *sulfides* and *organic matter* (e.g., fractions A3 and A6 and B3). Of the total bulk Se, the proportion in these two fractions reached 90% ($\sim 0.70\text{--}9.00\ \mu\text{g/g}$ or $\sim 120\text{--}3330\ \mu\text{g/g}$ in the Chinese samples). This is consistent with the data from the Cr(II)Cl₂ reduction (Table 1). The UK/ Colombian samples that contain between 1% S and 3% S, between 21% and 75% of the bulk Se was associated with the sulfides, thus clearly demonstrating that sulfides constitute the main pool of Se in this sample set (Matamoros and Benning, 2010). In contrast, the Chinese samples, have a much lower percentage of Se in the sulfides extracted by the Cr(II)Cl₂ treatment (0–18%) indicating that the majority of the Se in these samples is associated with the organic C fraction. (Table 1).

The Se concentrations extracted in the *elemental selenium* and *acetic acid soluble* fractions were very low in all samples ($\sim 0.1\text{--}7\%$). An association between Se and *oxide* fractions (B2 in Fig. 1) was observed only in the Chinese samples accounting for between 2% and 27% of the total bulk Se.

The sequential extraction data (both A and B protocol) show that in weathering environments characterized by slightly acid to neutral pHs, Se can be easily released from the shale (e.g., *water soluble* and *exchangeable* fractions). This can result in low concentrations of Se from waters associated with the UK/Colombia sample set ($\sim 0.02\text{--}0.40\ \mu\text{g/g}$), but in the Chinese sample set this can reach harmful values of up to $200\ \mu\text{g/g}$ in ground and thus irrigation waters. In the Yutangba province in China (Zhu et al., 2006) high Se concentrations in crops led to a serious Se-poisoning incident

for the inhabitants, with values in the irrigated soils and corn reaching between 3 and $10\ \mu\text{g/g}$ (note dietary reference intake for average person is $55\text{--}75\ \mu\text{g/day}$; WHO, 1996).

So far only a few studies have described the distribution of Se in shales using sequential extraction methods (e.g., Kulp and Pratt, 2004; Zhu et al., 2006). Generally, the present results support the previous findings and confirm that Se in shales is mostly linked to the organic and sulfide host phases. However, the sequential extraction protocols applied in the literature studies differ among each other, and only two record or quantify directly the association between Se and the sulfide fraction. In contrast, the current study demonstrates that only a combination of the chromous chloride reduction with both sequential protocols can clearly differentiate and separate the proportions of Se present in the sulfide versus the organic pools.

Lastly, the high concentrations of Se associated with the Fe–Mn oxides in the Chinese samples (between 4 and $\sim 500\ \mu\text{g/g}$) are particularly important because these poorly ordered oxides are sensitive to redox gradients and can transform to crystalline oxides at oxic–anoxic boundaries (Cornell and Schwertmann, 1996). These redox processes will affect the mobility and speciation of Se, although Se will also be released with increasing pH (i.e., Se desorption occurs above pH 4.0 on these oxides; Balistrieri and Chao, 1990).

In summary, the data clearly showed that in all studied shale samples, the prime Se host phases were organic matter and sulfides. Selenium was preferentially associated with organics only when the C% was very high and pyrite (S%) was absent or very low. However, in the presence of even small quantities of pyrite, the proportion of Se associated with this fraction became dominant and its association with the organic matter diminished in importance.

These results have implications both for the understanding of shale formation and also of shale weathering processes, which deliver Se back to the environment and potentially lead to Se-poisoning problems.

The reduced Se sequestered by organic matter and sulfides is thought to be due to microbial processes (e.g., Herbel et al., 2003). These two fractions both compete for any available Se but the substitution for S and thus incorporation of Se into pyrite

Table 1
Results from bulk selenium (Se), sulfur, carbon, Se-sulfides and XRD analysis.

Location	Selenium, sulfur and carbon data				XRD data						After chromous chloride reduction			
	Sample	Bulk Se (µg/g)	Inorg S (%)	Organic C (%)	Quartz (%) (normalized to sum to 100%)	Alumino-silicates (%) (normalized to sum to 100%)	Phyllo-silicates (%) (normalized to sum to 100%)	Pyrite (%) (normalized to sum to 100%)	Calcite (%) (normalized to sum to 100%)	Gypsum (%) (normalized to sum to 100%)	Se* (after Cr(II)Cl ₂) (µg/g)	Se** (µg/g)	Se*** (sulfides) (µg/g)	Se sulfides (%)
West Yorkshire, UK	S1	3.13	1.31	2.3	17.5	12.3	66.4	1.6	2.2	–	1.16	1.98	1.57	50.1
	S2	9.77	1.28	1.9	17.6	11.8	66.7	1.7	2.2	–	2.27	7.50	7.22	73.9
	S3	1.29	1.60	3.5	4.8	17.8	64.1	2.5	3.3	6.6	0.58	0.72	0.59	45.5
	S4	0.83	2.75	5.6	8.8	25.7	51.7	5.1	1.2	7.6	0.51	0.31	0.17	21.0
	S5	3.87	–	5.1	5.7	6.9	32.3	–	55.2	–	–	–	–	–
Villeta, Colombia Yutangba, China	S7	3.09	0.48	6.6	17.6	13.6	57.1	0.2	9.0	0.7	0.95	2.14	1.29	41.9
	S8	169	0.06	19.9	80.4	–	19.3	<0.2	–	0.3	194	–	–	–
	S9	1196	0.03	27.7	27.1	16.7	47.1	<0.2	6.2	2.9	1121	–	–	–
	S10	1525	0.06	13.1	70.8	2.6	19.1	<0.2	5.2	2.4	990	535	269	17.6
	S11	5254	0.06	14.2	76.3	3.7	18.8	<0.2	1.3	–	4615	639	142	2.7

Se* = Total Se in the remaining solid after the chromous chloride (Cr(II)Cl₂) treatment.

Se** = Bulk Se – Se*.

Se*** = Se** – Σ Se from fractions 1, 2, 4, 5 in protocol A.

Table 2
Distribution of selenium extracted with the two sequential extraction protocols (Protocol A: water soluble, ligand exchangeable, base soluble, elemental selenium, acetic acid soluble and residual. Protocol B: water soluble, hydrous Fe-Mn oxides, sulfides and organics and residual) in the samples from UK, Colombia and China.

Sample	Selenium (µg/g)													
	Protocol A (Kulp and Pratt, 2004; modified)						Sum of all fractions (1–6)	Recovery % ^a	Protocol B (Lussier et al., 2003)				Sum of all fractions (1–4)	Recovery % ^a
	Water Soluble A1	Ligand Exchangeable A2	Base Soluble A3	Elemental Se(0) A4	Acetic acid soluble A5	Residual A6			Water Soluble B1	Hydrous Fe- Mn Oxides B2	Sulfides + Organics B3	Residual B4		
S1	0.035	0.123	2.477	0.009	0.237	0.291	3.17	101.2	0.033	0.034	3.704	0.050	3.82	121.9
S2	0.109	0.121	6.506	0.049	0.000	2.801	9.59	98.1	0.100	0.065	9.434	0.070	9.67	98.9
S3	0.003	0.080	0.710	0.026	0.018	0.245	1.08	83.6	0.004	<DL	0.997	0.210	1.21	93.6
S4	0.003	0.070	0.273	0.022	0.044	0.488	0.90	108.8	0.003	<DL	0.779	0.020	0.80	97.0
S5	0.024	0.093	3.467	0.050	0.019	0.170	3.82	98.8	0.049	<DL	3.627	0.110	3.79	97.9
S7	0.267	0.388	2.556	0.154	0.031	<DL	3.40	110.0	0.186	0.243	0.868	1.710	3.01	97.4
S8	5.45	8.06	42.21	5.93	1.08	126	189	111.5	20	4.15	121	32	177	104.6
S9	65	115	500	79	4	594	1356	113.3	125	183	1066	48	1422	118.9
S10	78	97	409	88	3	966	1641	107.6	158	512	1149	18	1837	120.4
S11	183	222	941	89	3	4134	5572	106.1	196	281	3330	1501	5309	101.0

DL (detection limit): 0.4 µg Se/L; 0.0005 µg/g.

^a Recovery % = (sum of all fractions * 100)/Bulk Se (Table 1). The high [Se] in samples S8–S11 made quantification extremely difficult necessitating large and multiple dilution steps. Nevertheless, our results show that each sequential extraction step was successful, yielding satisfactory recovery percentages.

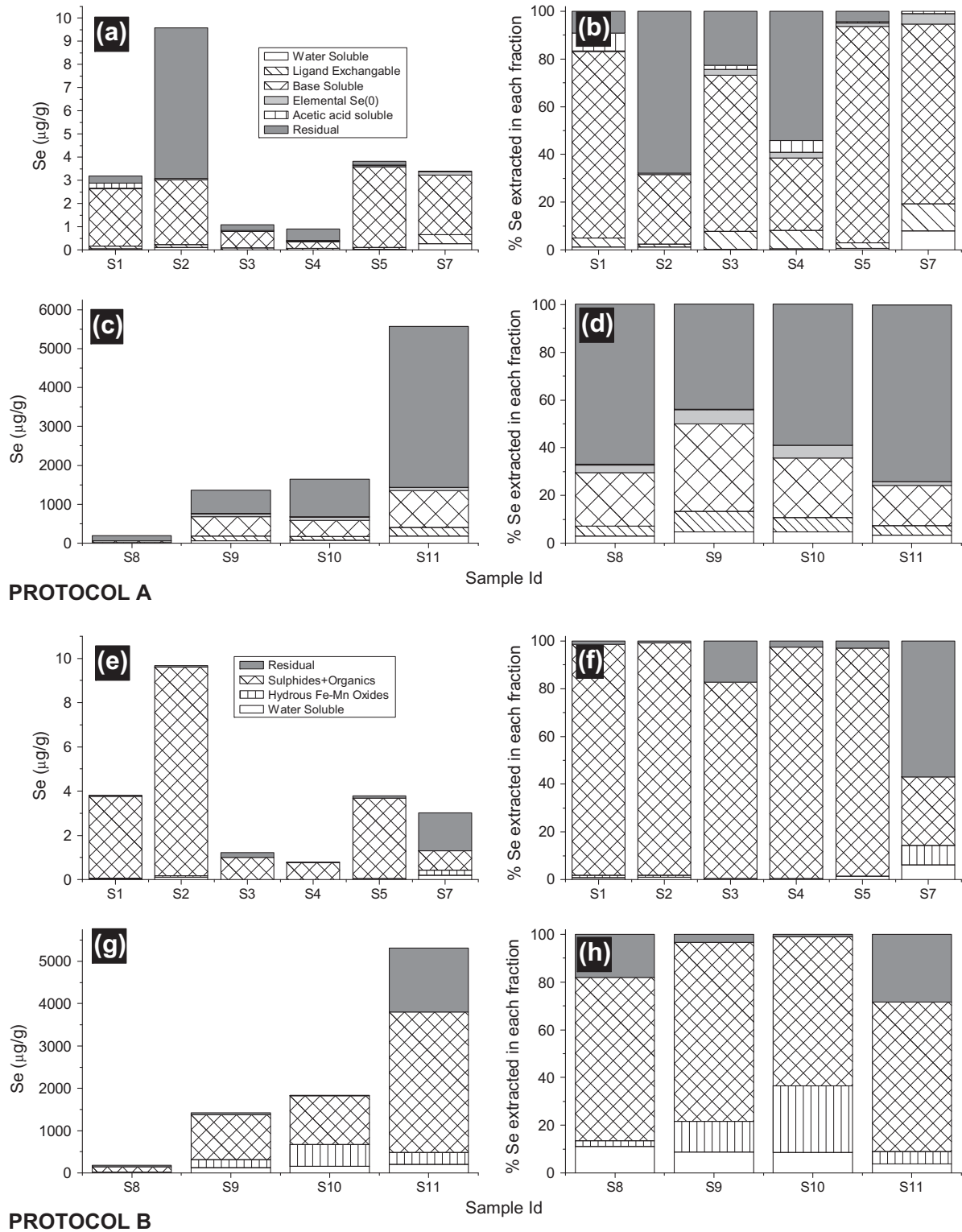


Fig. 2. Distribution of selenium in the two protocols applied, (left) in concentration (µg Se/g), (right) in percentage. (a, b, e, and f) UK/Colombia samples; (c, d, g and h) Chinese samples.

(Coleman and Delevaux, 1957) is much more rapid than its incorporation into organic matter. Furthermore, in organic rich marine sediments, pyrite formation is limited by the availability of reactive Fe and hence this is the ultimate control on the partitioning of Se between organic matter and sulfides. In both these hosts, Se becomes insoluble and immobile.

However, during oxidative weathering, the Se trapped in these hosts can become remobilized and released and be made bioavailable (e.g., Masscheleyn et al., 1990). This is particularly true for pyrite because its oxidation will not only release the trapped Se, but will also decrease the pH. Thus pyrite oxidation will also induce the dissolution of silicates, carbonates and Fe-Mn oxides,

and release additional Se from these host minerals. Chang and Berner (1999) compared the oxidation rates of pyrite and organic matter and revealed that pyrite oxidizes ~2–3 orders of magnitude faster. Therefore, in sediments with significant concentrations of Se linked to sulfides, the weathering of pyrite will constitute the most immediate source of Se to ground waters, and the reactions involved in this process will control the geochemistry of Se in these settings.

4. Conclusions

The prime host phases of Se in shales are organic matter and pyrite (~90%). However, Se will preferentially partition into pyrite even when it is present in relatively low concentrations (~1–3% S). Therefore, in the weathering of pyrite bearing sediments its oxidation will control the geochemical cycling of Se because:

- (1) The large proportion of Se contained in pyrite.
- (2) Pyrite oxidation will promote its release from other Se pools by the release of acidity.
- (3) Pyrite oxidizes faster than organic matter, which forms the other large Se reservoir in such sediments.

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