

Introduction

Aluminium is a member of group 13 of the periodic table, which also includes B, Ga, In and Tl. The element has an atomic number of 13, an atomic mass of 27, one oxidation state (+3) and one naturally occurring isotope (^{27}Al). The geochemical behaviour of Al is very similar to that of its group neighbour Ga.

Aluminium is a lithophile element and is the most abundant metal in the lithosphere, forming several of its own minerals, including sillimanite Al_2SiO_5 , corundum Al_2O_3 and kaolinite $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$. It is exceeded in abundance only by oxygen (45.5%) and silicon (25.7%) (Ildefonse 1999). It is a major constituent in many rock-forming minerals, such as feldspar, mica, amphibole, pyroxene and garnet. The weathered products of primary Al minerals include secondary clay minerals, *e.g.*, kaolinite and dioctahedral smectite, and Al-hydroxides, such as gibbsite, nordstrandite and bayerite, which may control the equilibrium concentration of Al in soil solution, groundwater and stream water. In tropical conditions, weathering may produce the Al-ore bauxite, a mixture of several secondary hydroxide/oxide minerals. Aluminium is present at percent levels in most of the common rock types, and has an average crustal abundance of about 8.3% (Ildefonse 1999).

Metamorphic rocks show both the widest variation, and the highest mean values with respect to Al_2O_3 concentration. Average values typically range from 12 to 24%, although Al_2O_3 concentrations as low as 1%, and as high as 28%, have been reported. With the exception of shale, sedimentary rock types commonly contain very little Al_2O_3 with average contents ranging from <1% to a maximum of 2.5% in carbonates and ~5% to 8% in sandstone. Shale contains much higher concentrations of Al_2O_3 , typically up to 15%, due to the presence of clay minerals such as kaolinite. Concentrations in igneous rocks generally increase with decreasing Fe and Mn content; ultramafic rocks such as peridotite contain as little as 4% Al_2O_3 , whilst mafic rocks such as basalt can contain up to 16%. Acid igneous rocks on average have Al_2O_3 concentrations in the range 15 to 25%, the higher values corresponding to igneous rocks rich in

feldspar, such as anorthosite and nepheline syenite (Wedepohl 1978) and late tectonic peraluminous granite in the Variscan basement (Faure *et al.* 2004). McLennan and Murray (1999) quote average values for river particulates and loess as 9.4 and 6.9% Al respectively.

Although most naturally-occurring Al resides in feldspar minerals and their weathering and alteration products, Al tends to correlate with elements such as Fe, Cr and V in weathered material, and can be used, therefore, as an indicator for the presence of mafic rocks.

Aluminium has a low mobility under most environmental conditions, although below pH 5.5 its solubility increases as it is released from silicate rocks (Shiller and Frilot 1996). Because of its amphoteric nature, aluminium may also be mobilised in anionic form under strongly alkaline conditions at pH values above 8 (Shiller and Frilot 1996). The speciation of aqueous Al is dependent on both pH and the presence and nature of complexing ligands. In the absence of significant concentrations of complexing ligands, the dominant form of dissolved Al below about pH 4.5 is Al^{3+} (Martin 1992). Above pH 4.5, the hydrolysed forms $\text{Al}(\text{OH})^{2+}$ and $\text{Al}(\text{OH})_2^+$ account for a significant amount of the total dissolved aluminium. At low pH, organic ligands, including humic and fulvic acids, and inorganic ligands, such as fluoride, readily complex with dissolved aluminium, and can increase its equilibrium solubility in solution. Dissolved organic carbon affects the release of Al through complex formation in the upper soil layer, while other mechanisms operate in the lower B-horizon (Kabata-Pendias 2001). Soil acidification arising from atmospheric deposition of S (mainly SO_2), also increases Al solubility in soil, possibly by the formation of soluble $\text{Al}(\text{OH})\text{SO}_4$. Oxidation of sulphides, *e.g.*, pyrite, in soil gives rise to the production of H_2SO_4 , which interacts with other minerals to produce Al ions that occupy exchange sites. The average total concentration of Al in global soil is reported as $80,000 \text{ mg kg}^{-1}$ (Koljonen 1992, Reimann *et al.* 1998).

As a result of organic complexation, particularly through chelation, a significant proportion of Al in stream water is usually

transported in colloidal or particulate forms. Concentrations of dissolved Al are generally low in most natural water, because of the low solubility of Al-bearing minerals under near-neutral pH conditions. Stumm and Morgan (1981, 1996) report a median concentration of $11 \mu\text{g l}^{-1}$ for Al in terrestrial water.

Anthropogenic sources of Al include aluminium smelters, cement plants, sewage and dust (Reimann and de Caritat 1998), but the natural background is usually dominant.

Aluminium is considered to be a non-essential element. Dissolved cationic aluminium is known to be toxic to various species, including fish,

invertebrates and plants. Its toxicity depends on its form in solution, *e.g.*, Al is more toxic to fish as the Al^{3+} ion than if it is complexed (Driscoll *et al.* 1980). Silicon and Ca have been shown to afford some protection to aquatic vertebrates and humans against the toxicity of Al (Birchall *et al.* 1989, Exley *et al.* 1997). Alzheimer's disease is associated with higher than normal amounts of Al in the brain, but it is now thought that this is a consequence, not a cause, of the disease (WHO 1996).

Table 8 compares the median concentrations of Al in the FOREGS samples and in some reference datasets.

Table 8. Median concentrations of Al in the FOREGS samples and in some reference datasets.

Aluminum (Al_2O_3)	Origin – Source	Number of samples	Size fraction mm	Extraction	Median %
Crust ¹⁾	Upper continental	n.a.	n.a.	Total	15.4
Subsoil	FOREGS	788	<2.0	Total (XRF)	11.7
Topsoil	FOREGS	845	<2.0	Total (XRF)	11.0
Soil ²⁾	World	n.a.	n.a.	Total	11.2
Water (Al)	FOREGS	807	Filtered <0.45 μm		17.7 ($\mu\text{g l}^{-1}$)
Stream water (Al) ³⁾	World	n.a.	n.a.		160 ($\mu\text{g l}^{-1}$)
Stream water (Al) ⁴⁾	Barents region	1364	Filtered <0.45 μm		49.1 ($\mu\text{g l}^{-1}$)
Stream sediment	FOREGS	850	<0.15	Total (XRF)	10.3
Floodplain sediment	FOREGS	749	<2.0	Total (XRF)	10.4

¹⁾Rudnick & Gao 2004, ²⁾Koljonen 1992, ³⁾Ivanov 1996, ⁴⁾Salminen *et al.* 2004.

Al_2O_3 in soil

The median Al_2O_3 content is 11.7% in subsoil and 11.0% in topsoil, with values ranging from 0.21 to 27.1% in subsoils and 0.37 to 26.7% in topsoils (Figure 1). The average ratio topsoil/subsoil is 0.925 (Table 4).

The Al_2O_3 subsoil distribution map shows low values (<7.68%) throughout the sandy plains extending from the Netherlands over northern Germany and Denmark to Poland and Lithuania, as expected because of the glacial sand and loess cover. Low values also occur in Ireland, the Paris and Garonne basins in France, central Hungary and eastern Spain, over mainly calcareous rocks.

High Al_2O_3 values in subsoil (>14.5%) occur throughout the western Iberian Peninsula, where

granitoids and Proterozoic and Palaeozoic schist of the Iberian Massif, as well as granitic rocks of Peñas de Aya (western Pyrenees), provide a substrate rich in feldspar and phyllosilicate minerals (mica and clay). The same general type of geology is present from the Central Massif to Brittany in France, on the island of Corsica, in south-west England, Wales, western Scotland, western Norway, northern Fennoscandia, the eastern Alps, and the Carpathians of Slovakia (crystalline and shale-rich Palaeozoic rocks together with Palaeogene to Neogene clayey sediments) - all in which Al_2O_3 shows positive anomalies. In Slovenia, west Croatia, and parts of western and northern Greece, Al_2O_3 enrichment

occurs in soils on carbonate rocks of karst areas, after CaO has been leached from soil. In north-eastern Greece, Al₂O₃ enrichment results from weathering of granite and granodiorite intrusions, gneiss and shale. In western Italy (Lazio and Tuscany), the high Al₂O₃ concentrations are explained by the presence of alkaline volcanic rocks with high alumina content. Weathering of Palaeozoic terrains and Al-hydroxide formation in soil causes high concentrations in south Portugal.

The Al₂O₃ topsoil distribution map is very similar to the subsoil map. Notable differences are a relative depletion in eastern Slovakia (smaller amount of clay minerals) and a higher alumina content in the eastern Pyrenees (schist and granite), the Baetic Cordillera (south-east Spain, related to schist and shale in Nevado Filábride Complex, as well as alkaline and calc-alkaline volcanism), and residual accumulations

of Al in karstic areas by leaching of Ca in central-south Spain.

Among the many elements that substitute for Al is Ga, which has the same charge and a similar ionic size. The correlation coefficient between Al₂O₃ and Ga is very strong (0.96 for subsoil and 0.97 for topsoil), and their geographical distribution is nearly identical.

Further significant correlations of Al in subsoils include a strong correlation (>0.6) with In, Fe, Sc, V, Ti, Nb, Ta, K, Rb, and most REE, and a good correlation (>0.4) with Th, U, Y, Be, Ba, Co, Zn, Pb, Ag, Bi, Cs, Tl and Mn. This pattern obviously underlines the importance of clay minerals in the distribution of these elements.

The pattern is the same for topsoil with minor shifts in the values of the correlation coefficients; the correlation of Al with Pb and Ag is much lower in topsoil than in subsoil.

Al in stream water

Aluminium values in stream water range over three orders of magnitude from <0.1 to 812 µg l⁻¹ (excluding three outliers up to 3370 µg l⁻¹), with a median value of 17.7 µg l⁻¹. Aluminium is correlated with iron and very closely inversely correlated with pH. The Al distribution pattern in stream water is controlled strongly by pH, with highest concentrations in the most acid environments of most of southern and central Fennoscandia and Ireland, and lowest concentrations in the areas adjacent to the Mediterranean. It is most similar to the REE and related elements pattern in stream water with low mineralisation and high DOC.

Patterns in stream water Al data are markedly different from distributions in the solid sample media, indicating predominance of exogenic factors (topography, climate, vegetation) over bedrock geology control for Al in streams.

Lowest Al values in stream water (<6.5 µg l⁻¹) are predominantly found in parts of northern France and north-eastern Germany, the central and eastern Iberian Peninsula, in a belt from south-east France through northern Italy, Slovenia to Croatia, in Albania and throughout most of Greece. Aluminium is not solubilised because of the relatively high pH in these areas, which is predominantly controlled by carbonates. In northern Fennoscandia, pH is relatively elevated by higher concentrations of buffering base cations

in soil (greenstone and deeply weathered bedrock in the ice divider area) resulting in low aluminium mobility. Low values of Al in central Sweden are related to elevated pH, an influence from Palaeozoic carbonates in western Scandinavia.

Highest Al values in stream water (>339 µg l⁻¹) are predominantly found throughout central and southern Fennoscandia and Denmark. These regions have base-poor buffering capacity because of their geology, and Al solubility is strongly controlled by acid pH. Anomalously high isolated Al values in southern Tuscany and Basilicata regions of Italy are related to the alkaline volcanic Roman Province and Vulture volcanoes respectively. The high Al values in northern Germany are associated with low pH values and high DOC, lanthanum, cerium and REEs, but Al is low in stream sediment. In south-central Spain a highly anomalous Al value is related to acidic conditions in the mineralised area of Valle de Alcudia. High values in Galicia (north-west Spain) are related to As (Au) mineralisation in or close to N-S shear structures.

A more detailed description on the chemistry of Al in stream water is given in Annex 1 of this volume by Ander *et al.* (2006), where the thematic interpretation of stream water chemistry is discussed (see section on Al and Si speciation and solubility).

Al₂O₃ in stream sediment

The median Al₂O₃ content in stream sediment is 10.4% , with values ranging from 0.2 to 25.9%.

The Al₂O₃ stream sediment distribution map shows low values (<6.7%) over the sandy plains extending from the Netherlands over northern Germany and Denmark, to Poland and the Baltic States, because of the fluvial, glacial and loess cover. Most of the Mesozoic-Cenozoic sedimentary basins of France are also low in Al₂O₃, as is the calcareous west of Ireland and parts of eastern and southern Spain.

High Al₂O₃ values in stream sediment (>13.4%) are found throughout the western Iberian Peninsula, where crystalline and shale-rich Palaeozoic rocks provide a source area for feldspars and phyllosilicate minerals (mica and clay). The same general lithology gives rise to high values in the Pyrenees, the Central Massif

and Brittany in France, Corsica and Sardinia, south-west England, Wales and northern England, western Norway, southern Finland (over clay-rich marine sediments), eastern Bavaria and the Czech Republic, eastern Slovakia, the central Alps, and northern Greece. In Gran Canaria (the Canary Islands) and north-east Sicily, high Al₂O₃ is related to weathering of basaltic rocks. Further high Al₂O₃ values occur in northern Croatia and parts of Italy. In the Roman magmatic province, high Al₂O₃ values are related to alkaline volcanic rocks.

In stream sediment, Al₂O₃ has a very strong correlation with Ga (0.93), a strong correlation with V, K and Rb, and a good correlation with Be, Li, Nb, Ta, Eu, Tl, Na, Ba, Ti, Fe, Co and Cu. There is a good negative correlation with CaO (-0.43).

Al₂O₃ in floodplain sediment

The distribution of total Al₂O₃ values in the floodplain sediment shows a marked variability ranging from 0.1 to 32.6%, with a median of 10.4%.

The most extensive area with low values of Al₂O₃ (<6.35%) is found in the glacial drift covered plains extending from northern Germany, the whole of Poland to most of the Baltic countries; over the calcareous rocks of Ireland, and eastern Spain, alluvial plains of the lower Seine, Garonne and Rhône rivers in France, and the molasse basin of central Austria.

High Al₂O₃ values in floodplain sediment (>12.9%) are characteristic of areas with granite, gneiss, schist, calc-alkaline and alkaline rocks. They occur in Fennoscandia (granite and gneiss of the Fennoscandian Shield and crystalline rocks of the Caledonides), Scotland (gneiss, schist, granitoids), Wales (schist, shale, felsic igneous rocks) and south-west England (granite), in France the Massif Central to the Armorican Massif in Brittany (granite), the Pyrenees (granite), central and western Iberian Peninsula (crystalline and shale rich Palaeozoic rocks), Sardinia (calc-alkaline and shoshonitic volcanics), Corsica (alkaline volcanics), Italian-Swiss Alps (granite), central-west Italy (Roman alkaline

volcanic province) and Calabria (alkaline intrusives), north-eastern Greece (Rhodope and Serbomacedonian Massifs with gneiss, schist, shale and granite), Croatia (residual clay in karst and clay-rich sediment), Slovenia (residual clay in karst), the crystalline rocks of southern Austria, eastern Hungary (Neogene clastics), and western Czech Republic (crystalline rocks of the Bohemian Massif). In Southern Finland and Sweden floodplain sediments were collected from drainage basins dominated by old marine clays from earlier phases of the Baltic Sea. Abundance of clay and mica minerals in the sediment explains the relatively high Al content.

The highest value in floodplain sediment, an outlier with 32.6% Al₂O₃ occurs in Cornwall (Hercynian granite), south-west England; it is also an outlier for Ga (52 mg kg⁻¹).

In floodplain sediment Al shows a very strong correlation with Ga (0.92), a strong correlation (>0.6) with Th, Rb, K, V, Ti, Fe, Nb, Ce, La, Y, Eu, Gd, Nd, Pr, Tb and Sm, and a good correlation (>0.4) with the other REEs and with Na, Li, Be, Ta, Tl, Co and U.

In conclusion, the spatial variation of Al₂O₃ in floodplain sediment is related to the bedrock geology (granite, gneiss, schist, calc-alkaline and

alkaline rocks, shale), but also to the distribution of clay-rich soil. As shown by the histograms, most of the Al_2O_3 values vary between 0.1 and

20%, with very few samples having higher concentrations.

Al comparison between sample media

Patterns in Al distribution between all solid sample media are broadly similar, although lower Al is present in stream sediment throughout the coastal region of Croatia and Slovenia (possibly because of the removal of fine-grained material from the residual soil and karst). In the southern tip of Finland and in parts of Britain, higher Al is observed in stream sediment than other solid sample media. A boxplot comparing Al variation in subsoil, topsoil, stream sediment and floodplain

sediment is presented in Figure 1.

Patterns in stream water Al data are markedly different from distributions in solid sample media and are controlled strongly by pH and DOC, pointing to prevalence of climate over geogenic control for Al in stream water. The highest Al concentrations occur in very acid environments of most of southern and central Fennoscandia and Ireland, and lowest concentrations in alkaline areas adjacent to the Mediterranean.

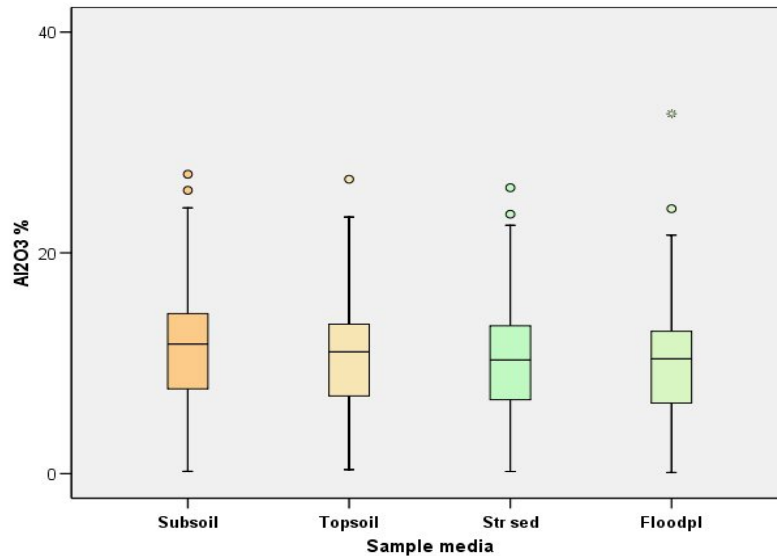


Figure 1. Boxplot comparison of Al variation in subsoil, topsoil, stream sediment and floodplain sediment.