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Acid Neutralization and Sulphur retention in S-impacted Andosols

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MAY 2005

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This Chapter is also adapted from

Delfosse T., Elsass F. & Delvaux B. 2005. Direct evidence of basic aluminium sulphate minerals in an S-impacted Andosol. *European Journal of Soil Science*, 56, 281-286.

Available on : <http://www.blackwell-synergy.com/rd.asp?code=EJS&goto=journal>

Chapter 7

Direct Evidence of Basic Aluminium Sulphate Minerals in Soil*

Summary

The formation of basic aluminium sulphate (BAS) minerals $[(K,Na)_n-Al_x(OH)_y(SO_4)_z]$ has often been invoked to explain sulphate retention in soils. These minerals have not yet, however, been directly observed in the soil. We extracted the clay fractions of Andosols intercepting large inputs of volcanogenic sulphur dioxide and acids (HCl, HF), simply by dispersing clays with Na^+ -resins in deionised water without any other chemical treatment. Clay fractions concentrate 39 to 63% of total sulphur content of soil. Transmission electron microscopy coupled with energy-dispersive analysis revealed the presence of BAS particles, appearing as nodules and spheres. These particles have an equivalent diameter smaller than 0.2 μm . They have an Al:S ratio close to 2.2 and 3.8 and are possibly amorphous aluminite or basaluminite, respectively. They seem to have been formed in microenvironments enriched in sulphate, but also in fluoride anions. Their formation seems to have been enhanced by the combination of large inputs of acids and SO_2 and an effective Al supply from weathering of volcanic glass.

*Adapted from Delfosse T., Elsass F. & Delvaux B. 2005. Direct evidence of basic aluminium sulphate minerals in an S-impacted Andosol. *European Journal of Soil Science*, **56**, 281-286.

7.1 Introduction

As suggested by Adams & Rawajfih (1977), the formation of basic aluminium sulphate (BAS) minerals $[(K,Na)_nAl_x(OH)_y(SO_4)_z]$, also named hydroxy aluminium sulphate, may contribute to sulphate retention in soils. Indirect proofs based on soil solution data support this hypothesis. Direct evidence of the occurrence of BAS minerals in soils is, however, still lacking.

The presence of BAS minerals in soils has been generally inferred from studies involving geochemical modelling (e.g. Courchesne & Hendershot, 1990; Wolt *et al.*, 1992; Agbenin, 2003) or selective extraction of sulphate (chapter 6). Alunite $[KAl_3(SO_4)_2(OH)_6]$, basaluminite $[Al_4SO_4(OH)_{10}.5(H_2O)]$ and jurbanite $[AlSO_4OH.5(H_2O)]$ were predicted to form according to calculations based on soil solution composition from a large variety of soil environments: acid sulphate soils (van Breemen, 1973), forest soils (e.g. Courchesne & Hendershot, 1990; Prietzel & Hirsch, 2000; Mayer *et al.*, 2001), soils fertilised with S (Hue *et al.*, 1985), and ones exposed either to marine aerosols (Hue *et al.*, 1990) or to S from volcanogenic deposition.

Despite numerous attempts to identify BAS in soils, these minerals have not yet been detected in them. In soils, SO_4^{2-} -bearing minerals are generally present as compounds of Ca, Ba, Na, Mg and Fe, e.g. gypsum $[CaSO_4.2H_2O]$ in gypsisols, barite $[BaSO_4]$ in acid sulphate soils (Hanor, 2000), Na_2SO_4 and $MgSO_4$ salts in evaporites on soils (Keller *et al.*, 1986), and schwertmannite $[Fe_8O_8(OH)_6SO_4]$ and jarosite $[KFe_3(SO_4)_2(OH)_6]$ in acid sulphate soils or in soils affected by acid mine drainage (e.g. van Breemen & Harmsen, 1975; Bigham *et al.*, 1996; Sùcha *et al.*, 2002).

The formation of BAS minerals is essentially determined by pH and the activities of Al and SO_4^{2-} in soil solution (Nordstrom, 1982), and is favoured by a SO_4^{2-} -rich solution in contact with a source of Al. These conditions are likely in young Andosols receiving volcanogenic acid and S, which may contain up to 6.6 g of SO_4^{2-} as BAS minerals per kg of soil (Chapter 6). In this paper, we report the results of a transmission electron microscopy study on clay fractions extracted from Andosols exposed to substantial deposition of acid and sulphur dioxide from Masaya volcano, Nicaragua.

7.2 Materials and methods

Four soil samples were selected on the basis of weathering stage and estimated BAS mineral content calculated from selective extraction data (Chapter 6) : VI2-2BC, EU2-A2, EU2-Bw and EU5-Bw1.

The clay fraction ($< 2 \mu\text{m}$) was separated with Na^+ -resin (Amberlite IR-120, Fluka) as dispersing agent (pH 6.2-6.5) and ultrasonic dispersion without any other chemical treatment (Rouiller *et al.*, 1972; Bartoli *et al.*, 1991). We quantitatively recovered the clay fraction by adding drops of saturated SrCl_2 solution to induce flocculation of clays. In a vitrified graphite crucible, 200 mg of clay sample was heated with a flame and allowed to glow red for 3 minutes in the presence of 1 g NaOH and 2 g Na_2O_2 . The cooled melt was dissolved in 30 ml HCl and total S was measured by Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES). X-ray diffraction ($\text{Cu-K}\alpha$, Bruker D8) was done on clay samples previously air-dried and oriented by drying off clay suspensions on ceramic plates. Transmission electron microscopy (TEM) was applied to clay samples embedded in Spurr resin as described by Elsass *et al.* (1998). Sections, 100 nm thick, were cut with a Reichert Ultracut Microtome fitted with a diamond knife. Electron microscope images and chemical analyses were obtained on a Philips 420 STEM microscope and an Oxford INCA energy-dispersive analytical system (EDS), respectively.

7.3 Results

The particle-size distributions of soils and the total S content of clay fractions are presented in Table 7.1. The clay content in the Eutric Andosols (37-52 %) was much larger than in the Vitric Andosol (4 %), in agreement with the more advanced weathering stage of the former. Total S content of the clay fraction in the Vitric sample (14.7 g kg^{-1}) was larger than in the Eutric Andosols ($3.3\text{-}4.4 \text{ g kg}^{-1}$). X-ray diffraction patterns of clay samples did not reveal any feature linked to crystal structure. Observations by TEM and EDS analyses revealed the common constituents of Andosols: allophanic constituents and poorly crystalline Fe-oxide. The chemical composition of these minerals indicates that they generally contain S, Cl and F.

Table 7.1: Total S content in soil (S_{soil}), organic carbon, allophane (Allo.) and ferrihydrite (Ferri.) contents in soils, particle-size distribution, total S in the clay fraction (S_{clay}) and relative contribution of clay to total S content of soil (CCSS).

Sample	S_{soil} /g kg ⁻¹	Org. C -----	Allo. /%	Ferri. -----	Particle-size distribution			S_{clay} /g kg ⁻¹	CCSS /%
					Clay -----	Loam /%	Sand -----		
VI2-2BC	1.6	1.0	2.9	1.3	4	14	82	14.7	39
EU5-Bw1	2.4	4.0	26.4	7.7	37	47	16	3.3	50
EU2-A2	2.3	8.1	17.7	7.1	42	46	12	3.4	63
EU2-Bw	4.3	5.8	29.4	11.1	52	32	15	4.4	53

Figure 7.1 illustrates the results of TEM for the Vitric Andosol VI2-2BC sample and the data from the EDS are listed in Table 7.2. In this sample, but not in the Eutric Andosol samples, some allophanic constituents (A) were surrounded by nodular particles (BAS) composed essentially of S and Al with traces of F, P, Cl, Si and Fe (Table 7.2). The Al:S ratio in BAS particles (2.2-3.8) was smaller than that of the associated A particles (43.5-144.8) and other A particles (26.7-54.8). The Al:Si ratio in BAS particles was the largest (11.0-12.4) and decreased in the following order: BAS particles > A particles (1.8-3.6) > volcanic glass (0.3). The F:Cl ratio was larger in the associated A and BAS particles shown in Figure 7.1 (16.3-71.3) than in A particles observed elsewhere (0.1-3.9).

7.4 Discussion

As illustrated in Figure 7.2, the efficacy of the Na⁺-resin procedure in extracting clays from strongly microaggregated soil material confirms previous results (Delvaux *et al.*, 1989; Bartoli *et al.*, 1991). Clay content is indeed strongly and negatively correlated ($r = 0.98$) with the Total Reserve in Bases (TRB), which is an estimator of the content of weatherable minerals in soils. Interestingly, the data from Masaya Andosols fit with the TRB-clay relationship established for other volcanic ash soils also derived from basalt, in Cameroon (Delvaux *et al.*, 1989).

Despite the small clay content in the Vitric Andosol, 38% of total S was stored in its clay fraction, which contained 14.7 g S kg⁻¹ clay. The lesser S-enrichment of the clay fraction in the Eutric Andosol was probably caused either by S storage in silt and sand fractions or by dissolution of the SO₄²⁻-phases following abundant washing during clay

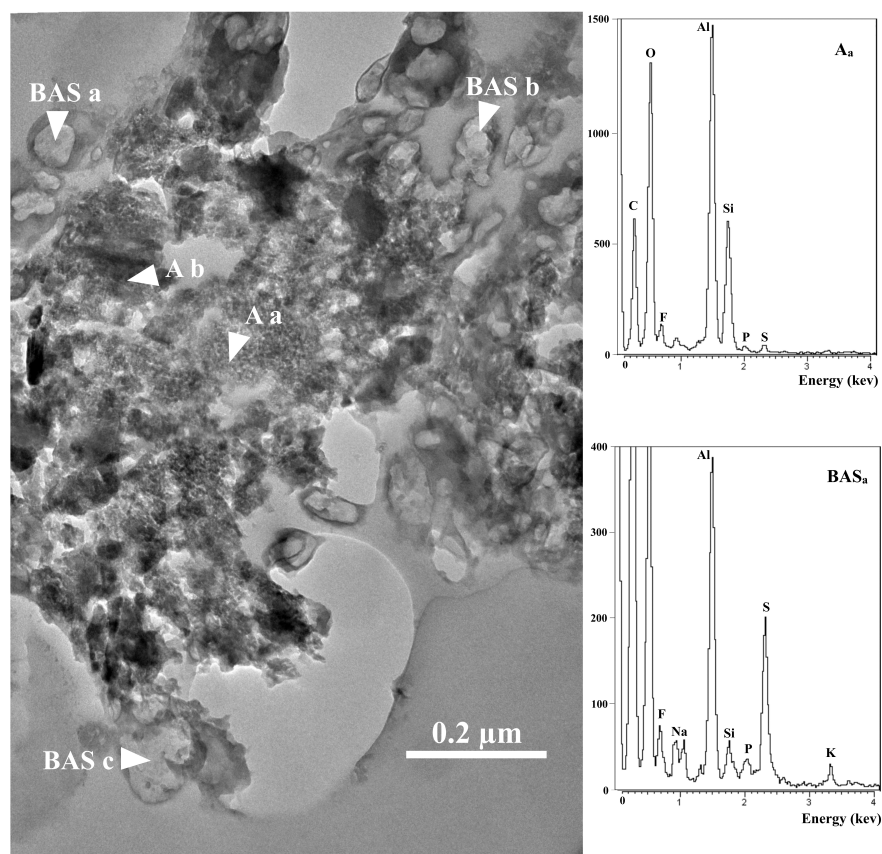


Figure 7.1: TEM micrograph of ultrathin section of the clay fraction of Masaya Vitric Andosol VI2-2BC sample and corresponding EDS analyses showing allophanic constituents (A) surrounded by basic aluminium sulphate (BAS) minerals. Arrows a, b and c correspond to analyses reported in Table 7.2.

Table 7.2: Atomic ratios of various elements analysed by EDS in VI2-2BC sample (Figure 7.1) and in Eutric Andosol samples.

Mineral phase		Atomic ratios							
		Al:S	Al:Si	Al:Fe	Al:F	O:Al	S:Cl	F:Cl	S:F
Aggregate particles (Figure 7.1)	¹ BAS ^a	2.2	11.0	16.4	4.1	3.9	30.8	16.3	1.9
	BAS ^b	3.8	11.0	15.0	4.8	2.2	31.5	24.6	1.3
	BAS ^c	2.2	12.4	16.9	1.8	3.5	54.6	66.2	0.8
	² A ^a	144.8	3.6	30.6	7.1	2.1	1.1	22.3	0.1
	A ^b	43.5	2.5	34.3	6.3	2.2	10.3	71.3	0.1
Other particles (not in Figure 7.1)	glass	28.3	0.3	1.2	17.0	11.6	1.5	2.5	0.6
	A	41.5	2.0	21.8	15.8	4.4	0.6	1.6	0.4
	A	38.5	2.0	25.2	182.8	3.4	0.4	0.1	4.8
	A	54.8	1.8	31.8	5.9	3.3	0.4	3.9	0.1
	A	26.7	2.0	12.8	9.1	4.7	0.8	2.2	0.3

¹Basic Aluminium Sulphate mineral²Allophanic constituents

a, b and c correspond to nodules arrowed in Figure 7.1

extraction. The Na⁺-resin procedure indeed required five times more water for Eutric soil than for the Vitric one.

The BAS particles in the Vitric clay samples were identified as basic aluminium sulphate minerals with Al:S ratios of 2.2 and 3.8. They may thus be either aluminite [Al₂(SO₄)(OH)₄.7H₂O] or a less hydrated compound such as meta-aluminite [Al₂(SO₄)(OH)₄.5H₂O], or basaluminite [Al₄SO₄(OH)₁₀.5(H₂O)], respectively. The BAS minerals appeared as nodules and spheres, very similar to the aluminite-like minerals observed in anoxic limestone drains by Robbins *et al.* (1996). The BAS particles were very small with an equivalent diameter < 0.2 µm (Figure 7.1).

The occurrence of BAS particles in an S-impacted Andosol rich in volcanic glass might have three origins: (i) formation inside the volcano and subsequent spread on to the soil after the volcano erupted, (ii) release as sulphate-bearing aerosols, and (iii) synthesis in soil.

Depending on oxydo-redox conditions, dissolved S in magma can be present as a metal-sulphide or a sulphate mineral phase. The only sulphate phase that has been shown to form in silicate melts is anhydrite (CaSO₄) (Bernard *et al.*, 1991; Wallace & Anderson, 2000). In contrast, alunite and jarosite may constitute secondary phases formed during acidic alteration of volcanic rocks by hydrothermal fluids (Hochstein & Browne, 2000). Such conditions are unlikely at Masaya volcano. The volcano has a long recorded history of shallow lava-lake activity (Rymer

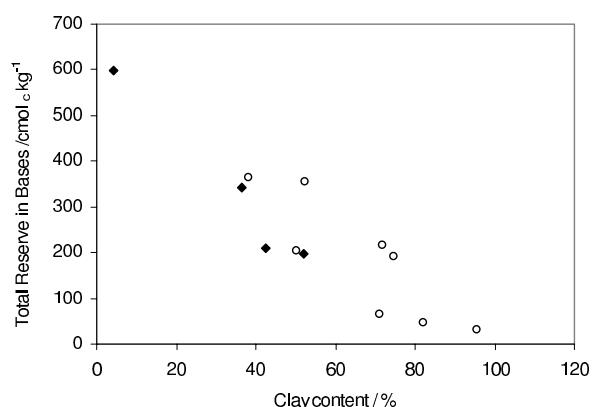


Figure 7.2: Relationship between the total reserve in bases (TRB) and the clay content for Masaya Andosols (◆) and Andosols from Cameroon (○; Delvaux *et al.*, 1989).

et al., 1998), which impedes the development of a sizeable near-surface hydrothermal system. In addition, there is no evidence for the presence of hydrothermal material in the tephra erupted by Masaya since the last caldera formed, about 6000 years ago (Williams, 1983; Rymer *et al.*, 1998). A potential contribution from a volcanic aerosol phase also can be discarded. Volcanic aerosols generally contain small concentrations of Al, and charge-balance considerations show that sulphate is present predominantly as sulphuric acid, ammonium sulphate, or K-, Na-, Ca-sulphate particles or several of them (Mather *et al.*, 2003). Thus, the best explanation for the presence of BAS in the Vitric clay samples seems to be precipitation in the soil, where weathering of the volcanic glass constitutes the major source of Al.

The Al:Si ratios of BAS particles (11.0-12.4) and A particles (1.8-3.6; Table 7.2) were larger than the ratio of volcanic glass (0.3). This indicated a large enrichment of Al with respect to Si, particularly in BAS particles. These particles were also specifically enriched in S as shown in Table 7.2 by the smaller Al:S ratio in BAS (2.2-3.8) than in allophanic constituents (26.7-114.8). The BAS minerals are likely to have formed in a microenvironment particularly enriched in volcanic acid and halogen since the F:Cl ratios in both BAS (16.3-66.2) and associated A particles in Figure 7.1 (22.3-71.3) were larger than those of A particles observed elsewhere (0.1-3.9; Table 7.2). Since allophanic constituents do form from glass weathering in soil and specifically fix fluoride against chloride (Shoji *et al.*, 1993), this feature further supports our hypothesis

of BAS synthesis in soil. Interestingly, anion occurrence in BAS particles was in the order $S > F \gg P > Cl$, in contrast to SO_4^{2-} -sorption by poorly crystalline constituents in soils, which generally follows the affinity order $F > P > S > Cl$. Thus BAS formation was not impeded by the occurrence of anions competing for chemisorption since S:P and S:F ratios in BAS particles exceeded by one order of magnitude those in A particles.

Surface precipitation, i.e. two-dimensional chemisorption followed by three-dimensional nucleation and precipitation (McBride, 2000; Figure 7.3) rather than direct precipitation from solution, may be the formation pathway of BAS particles in soil. The occurrence of BAS surrounding allophanic constituents may support this hypothesis, which might explain the detection of BAS in the Vitric sample only. The Vitric Andosols downwind from Masaya volcano met the full set of conditions prevailing for BAS formation. They intercept large quantities of volcanogenic acids and SO_2 like the Eutric Andosols do (Delmelle *et al.*, 2001), but they contain large amounts of highly weatherable volcanic glass, which constitute a much more effective source of Al than allophanic constituents; and they have a small surface area available for sorption of SO_4^{2-} (Chapter 3). In Eutric soils with large surface areas, BAS particles were indeed undetected by TEM. Besides, the dissolution of the SO_4^{2-} phases might have been enhanced in Eutric samples following clay dispersion, as mentioned above.

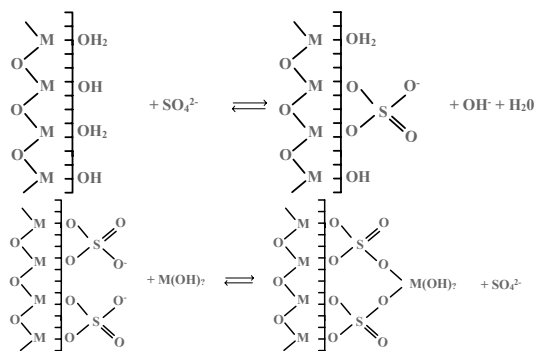


Figure 7.3: Surface precipitation of SO_4^{2-} , i.e. (a) two-dimensional-chemisorption followed by (b) three-dimensional-nucleation and precipitation (hypothetical pathway). Adapted from Ler & Stanforth (2003).

The soil solutions extracted from Masaya Andosols were oversaturated with respect to both basaluminite and alunite (Chapter 4). Unfortunately no thermodynamic data are so far available for alunite. However, the presence of alunite minerals is likely since their solubility does not significantly differ from that of basaluminite (Basset &

Goodwin, 1949). These minerals as well as meta-aluminite have been observed in close association (Fronzel, 1968).

The aluminite minerals group has been little studied, probably because Bassett & Goodwin (1949) failed to synthesise it. However, these authors successfully synthesised a less hydrated and amorphous compound $\text{Al}_2(\text{SO}_4)(\text{OH})_4 \cdot 4\text{H}_2\text{O}$. This solid might be one of those observed in Masaya Andosols (Figure 7.1) since it is amorphous as inferred by selective area electron diffraction (not shown). It is the least soluble aluminite compound, and precipitates from solution more readily than crystallised minerals (Nordstrom, 1982).

The Al:S ratio of BAS particles (2.2-3.8) was in the same order of magnitude as the one attributed to NH_4F -dissolved hydroxy aluminium sulphate (4.5) in the Vitric sample (Chapter 6). This supports the view that NH_4F solubilises BAS minerals in soil (Prietz & Hirsch, 2000).

The BAS minerals have a small size ($< 0.2 \mu\text{m}$) and seem to concentrate in the clay fraction of soils, particularly in microenvironments enriched in SO_4^{2-} where elevated acid concentration has favoured the liberation of Al. BAS minerals may thus be preferentially located in the fine clay fraction ($< 0.2 \mu\text{m}$) or may form on pyroclast substrate similarly to halloysite-smectite mixed-layer clays (Delvaux & Herbillon, 1995). Therefore, to further enhance the concentration of these minerals two methods are likely to succeed: (i) the extraction of the fine clay fraction ($< 0.2 \mu\text{m}$) or (ii) the collect of the clay fraction exposed to the highest ultrasonic dispersion time. This last procedure allow indeed to extract clay particles firmly aggregated onto or bound to larger particles (Delvaux & Herbillon, 1995).

To test these hypothesis, we (i) separated the clay fraction by ultracentrifugation in three fractions: $< 0.2 \mu\text{m}$, $0.2 < 1 \mu\text{m}$ and $1 < 2 \mu\text{m}$, and (ii) collected the clay fraction after successive ultrasonic dispersion time varying from 30" to 200' (i.e. 30", 2'30", 5', 25', 50', 100' and 200').

As shown in Figure 7.4 and 7.5, total S content in clay did not vary significantly with increasing exposure to ultrasonic waves nor with decreasing the fraction size. There is therefore no indication that BAS minerals concentrate in the fine clay fraction or form on pyroclast substrate. Precipitation would rather follow adsorption onto short-range ordered minerals, which may present various sizes. These results thus also plead for a surface precipitation mechanism rather than direct precipitation for BAS formation. The major condition favouring precipitation being therefore probably related to elevated soil SO_4^{2-} concentration.

Direct evidence of BAS in S-impacted soils was until recently lacking, probably because apparently amorphous minerals tend to form (Nordstrom, 1982). Moreover, secondary and neosynthesised minerals com-

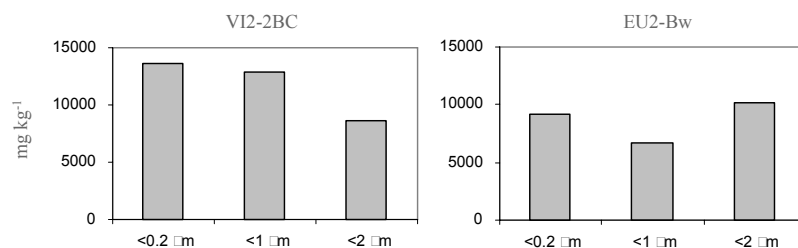


Figure 7.4: Total S content in the < 0.2 μm, 0.2 < 1 μm and 1 < 2 μm fractions of the VI2-2BC and EU2-Bw samples.

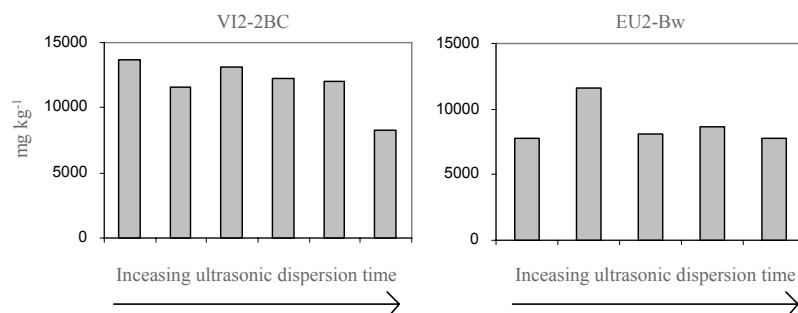


Figure 7.5: Total S content in the clay fractions collected after successive ultrasonic dispersion time varying from 30" to 200'.

monly concentrate in the clay fraction of soils. Therefore, increasing the probability of observing BAS minerals requires the extraction of the clay fraction without dissolution of the sparingly-soluble BAS minerals. The most common method used in particle-size analysis involves the use of specific reagents: hydrogen peroxide, sodium carbonate and sodium hexametaphosphate, which favour dissolution of BAS. The Na⁺-resin procedure has been successfully applied in Andosols by Delvaux *et al.* (1989) and Ndayiragije & Delvaux (2003). Clays are dispersed with Na⁺-resins in deionised water, i.e. in an aqueous medium with negligible ionic strength. Moreover, the procedure does not involve the use of any aggressive chemical agent.

From selective extraction data from Chapter 6, we estimate that the Andosols of the Masaya area contain 0.5 to 6.6 g of SO₄²⁻ as BAS minerals per kg of soil, which represents 10 to 50 % of total soil sulphate content. These results as well as the ones presented here suggest that the formation of BAS minerals plays a major role in sulphate retention

in S-impacted soils of the Masaya area.

This study opens new views in BAS minerals in soils. The well-adapted technique (Na^+ -resin extraction coupled with TEM and EDS) applied to soils where BAS minerals are likely to form (e.g. acid sulphate soil, S-polluted and S fertilised soils) would certainly help to understand the formation of BAS minerals and the fate of SO_4^{2-} in soils.

7.5 Conclusion

We extracted clays from acid- and S-impacted Andosols rich in weatherable volcanic glass. The extraction procedure involved dispersion with Na^+ ions in an aqueous medium of negligible ionic force. In these clays, we directly observed genuine particles of basic aluminium sulphate (BAS) minerals. We conclude that BAS minerals could form in these Andosols, because the soils intercept large inputs of acid and sulphur dioxide, and they contain huge reserves of weatherable volcanic glass acting as an effective source of Al. We believe that the combination of a well-adapted clay separation with TEM and EDS provided direct evidence of BAS minerals in soil. We also believe that our results open new ways to identify other hypothetical mineral phases in soils (e.g. arsenate-bearing phases), to confirm the occurrence of BAS minerals in other kinds of soils, and to help understand the mechanisms by which BAS forms in soils.

