1.5.O. Session I.

Micromorphology of salt accumulations in soils of north Monegros, Spain: optical microscopy and SEM.

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1. Introduction

Salt minerals in saline soils and salt crust have recently been the subject of an extensive review by Mees and Tursina (2010). In the region of Monegros (northeast Spain) accumulations of soluble salts have been studied by Pueyo (1978), López Mandado (2007), Vizcayno et al. (1995), and Mees et al. (2011). As a follow-up to previous work by Rodriguez-Ochoa et al. (1998) and Vizcayno et al. (1995); in this study, four areas affected by soil salinity were sampled in order to determine the mineralogy, morphology, formation conditions, and regional variations of the soil salt accumulations.

2. Materials and methods

Four sites (Grañen (GR), Torralba (TO), S. Lorenzo de Flumen (SLF) and S. Juan de Flumen (SJF)) were studied within the Flumen-Monegros irrigation district in the Monegros region within the Ebro Valley (south Huesca, NE Spain). At these sites, 69 surface salt accumulations were sampled in winter (28) and summer conditions (41). The climate, geology, geomorphology, hydrology, and general soils information of North Monegros is described in Rodriguez-Ochoa et al. (1998).

The mineralogical identification was performed using X-ray diffraction (XRD) with a Philips PW 1130 diffractometer. The mineral phases were identified with the aid of the Powder Diffraction File. Thin sections were described according to Bullock et al. (1985) and Stoops (2003).

Scanning electron microscope (SEM) studies, SE and BES modes, was performed with a Zeiss DSM 960 SE microscope equipped with an Oxford link 5118 energy dispersive X-ray spectrometer (EDS) microanalysis system.

3. Results and discussion

Results of the XRD mineralogy analysis of salt accumulations are presented in Table 1. In the TO site Mirabilite and Thenardite are predominant in the winter salt accumulations, and Thenardite, Bloedite and Halite in those developed during the summer. Konyaite, Epsomite and Eugsterite appear in minor proportions in winter conditions. Gypsum, Bloedite, Hexahydrite and Glauberite appear in both types of accumulations. The geochemical facies related to these minerals is Na-Mg-Cl-SO_4, based on chemistry of soils and groundwater.

Table 1. Mineralogical composition (XRD) of soil surface salt accumulations in North-Monegros

Loc.	Samples	Hl	Mb	Tn	Ky	Bl	Ys	Hx	Eps	Gb	Eug	Buk	Tr	Nt	Other
TO	Winter (11)	*	**	***	*	*	*	*	Tr	Tr	□	--	--	--	--
	Summer (6)	**	--	**	--	**	*	*	--	*	--	--	--	--	--
GR and SLF	Winter (11)	*	**	**	--	--	--	--	--	--	--	--	*	**	Apth
	Summer (23)	*	--	**	--	--	--	--	--	--	--	*	*	--	Ettr
SJF	Winter (6)	**	***	**	*	*	Tr	--	--	Tr	Tr	--	--	--	--
	Summer (12)	***	--	**	--	*	*	--	--	Tr	*	--	--	--	--

Loc.: location; TO: Torralba; GR: Grañen; SLF: San Lorenzo de Flumen; SJF: San Juan de Flumen. // Hl: Halite; Mb: Mirabilite; Tn: Thenardite; Ky: Konyaite; Bl: Bloedite; Ys: Gypsum; Hx: Hexahydrite;Eps:Epsomite; Gb: Glauberite; Eug: Eugsterite; Buk: Burkeite; Tr: Trona; Nt: Natron; Apth: Apthitalite; Ettr: Ettringite. //Asterisks indicate relative abundance; Tr. traces

In GR and SLF samples, XRD show that Mirabilite, Thenardite and Natron are the main mineralogical components in the winter efflorescences. Halite and Trona are present in lesser proportions. Thenardite, Halite, Burkeite and

Trona are presents in the summer salt accumulations. Apthitalite appears only in samples on sandstone outcrops and Ettringite on a brick fragment. The geochemistry facies of the soils and groundwater is Na-Cl-SO_4-CO_3.

The XRD of S. Juan de Flumen (SJF) samples show that Mirabilite, Halite and Thenardite are predominant in winter and Halite and Thenardite in summer. In less proportions appear Konyaite, Bloedite, Gypsum, Eugsterite and Glauberite in cooler season. Bloedite, Gypsum, Eugsterite and Glauberite appear in warmer season (Fig. 1). Geochemical facies related of this mineral are Na-(Mg)-Cl-SO_4 based in chemistry of soils and groundwater.

The natural salt minerals identified by optical microscopy, SEM-BSE SEM-SE and EDS microanalysis techniques are shown in Table 2. Here we will only briefly describe a few issues in relation to those minerals that have been identified for the first time in the region. Barite is common in these soils but in very small amounts. It has been identified in surface plough horizons, subsurface B and C horizons, textural crusts, and in siltation material of drainage systems (Rodriguez-Ochoa et al. 1998). It appears in the four sites studied, in saline-sodic soils with variable hydromorphic problems. SEM-SBE+ EDS is a very powerful tool for Barite and Baritocelestite observations.

Table 2. Minerals in salt accumulations in soils (Gr: Grañen; SJF: S. Juan de Flumen; SLF: San Lorenzo de Flumen; TO: Torralba).

Mineral	Chemical Formula	Morphology	Location
Barite	$BaSO_4$	Prismatic; tabular; clusters microlites	SJF-SLF-TO
Baritocelestite	$(Sr,Ba)SO_4$	Prismatic; tabular; clusters microlites	TO
Mirabilite	$Na_2SO_4 \cdot 10H_2O$	Elongated prismatic	SJF
Thenardite	Na_2SO_4	Pseudomorphic after Mirabillite with drusy-like pyramid crystals	GR-SJF-TO
		Rosette-like	GR-SJF-SLF
		Needle-shaped	SJF
		Lenticular	TO
		Nodular microcrystalline aggregates	GR
		Anhedral	SJF
		Microcrystalline	TO
Bloedite	$Na_2Mg(SO_4)_2 \cdot 4H_2O$	Prismatic subidiomorphic	SJF
		Anhedral	SJF-TO
		Globular microcrystalline	SJF-TO
		Prismatic-radial intergrowth	SJF-TO
		Anhedral cement	SJF
Konyaite	$Na_2Mg(S0_4)_2 \cdot 5H_2O$	---	SJF-TO
Halite	NaCl	Cubic, hopper, chevron	SJF-SLF
		Anhedral cement	GR-SJF-SLF
		Fibrous prismatic; acicular	SJF
Epsomite	$MgS0_4 \cdot 7H_2O$	Prismatic; tabular; microcrystalline acicular elongated parallel and radial	TO
Hexahydrite	$MgS0_4 \cdot 6H_2O$	Lath-shaped crystals, microcrystalline acicular elongated parallel and radial	TO
Trona	$Na_2CO_3 \cdot NaHC0_3 \cdot 2H_20$	Microcrystalline; lath-shaped, acicular; bars in radiating fans; prismatic	GR-SLF
Natron	$Na_2CO_3 \cdot 10H_20$	Prismatic subidiomorphic	GR-SFL
Thermonatrite	$Na_2CO_3 \cdot H_20$	Prismatic pseudomorphic after Natron	GR-SLF
Burkeite	$2Na_2SO_4 \cdot Na_2CO_3$	Book plate; prismatic	GR-SLF
Gypsum	$CaSO_4 \cdot 2H_20$	Lenticular; desert rose intergrowths; acicular	SJF-TO
Glauberite	$Na_2Ca(SO_4)_2$	Acicular; radial acicular aggregates	SJF-TO
Eugsterite	$Na_4Ca(SO_4)_3 \cdot 2H_2O$	Acicular; radial acicular aggregates; elongated prismatic needle euhedral/-subhedral	SJF-TO
Gaylussite	$Na_2Ca(CO_3)_2 \cdot 5H_2O$	Subhedral tabular; short prismatic; prismatic cuneiform	GR
Northupite	$Na_2Mg[Cl(CO_3)_2]$	Cilinder-like	GR
Ettringite	$Ca_6Al_2(SO_4)_3(OH)_{12} \cdot 26H_2O$	Microcrystalline neddles	GR
Aphthitalite	$K_3Na(SO4)_2$	Acicular microcrystalline	SLF (sandstones)
Calcite	$CaCO_3$	Nodular; microsparite; sparite	GR

The only previous reference to Celestobarite found in the literature is the wotk of Sullivan and Koppi (1995). In our study we have identified some soil accumulations of Baritocelestite (Fig. nº 4). The Sr/Ba ratio varies between 53,9 and 17,2 with an average of 34,6. The presence of Strontium is associated to Tertiary gypsum formations, which is the parent material of the sediments deposited in the valley bottoms, where Typic Haplosalids have developed in hydromorphic conditions and rice is a common crop. Baritocelestite has been identified only by SEM-BSE combined with EDS in TO samples.

The efflorescences of TO samples present Hexahydrite, identified by XRD and SEM-BSE combined with EDS. They have a micro crystalline fibrous morphology. Epsomite has an unstable behaviour during SEM Analysis and has only been identified by XRD. These two Mg-sulphate soluble salts are also related to gypsiferous Tertiary geological formations.

The distribution patterns of Glauberite and Eugsterite as minority minerals indicate their relation with gypsum evolution. They have been identified by XRD, optical microscopy and SEM-BSE combined with EDS (Figs.1 and 2) The change in these minerals after dehydration has been described by Buck et al. (2006). The needle acicular morphology agrees with Vergrouwen (1981), Mees and Stoops (1991), and Buck et al. (2006). Previously, only Gumuzzio and Casas (1995) had described the presence of pedogenic Eugsterite in Spanish soils.

Gaylussite, a sodium and calcium carbonate, has been identified in soils only in two occasions (Fig nº 3). It shows as subhedral morphologies, aggregated crystals and crystalline overgrowths, and has been identified in GR samples by optical microscopy and SEM-BSE combined with EDS.

An uncommon Na-Mg-S-O-Cl phase appears in GR samples and is provisionally identified as Northupite, its chemical formula being $Na_2Mg[Cl(CO_3)_2]$. Its morphology is cylinder-like with micro acicular crystals in the surface. It has been identified only by SEM-BSE combined with EDS.

Ettringite is a hydrous calcium-aluminium sulphate, but it is a man-made artifact that appears in a salt efflorescence in SLF over a brick fragment. It has been identified by XRD and SEM-BSE combined with EDS.

A few references have described aphthitalite (Mees and Tursina 2010). In our samples, it only appeared in sandstone outcrop. The typical morphology observed is microcrystalline efflorescence. In these soils, with predominant illite clays, potassium disappears by retrogradation in the crystalline structures of illite. This mineral has been identified by XRD and SEM-BSE combined with EDS.

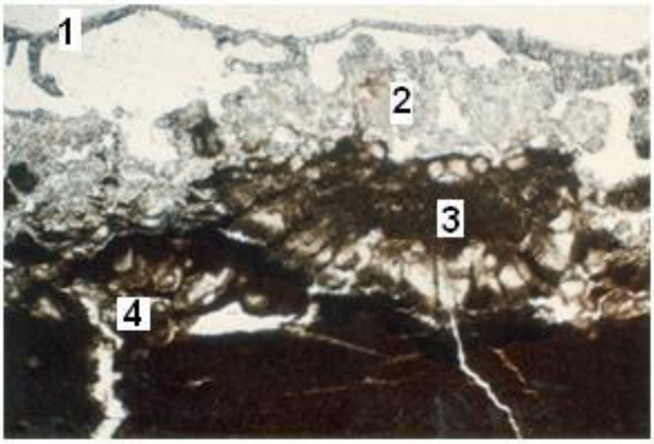

Figure 1. Salt crust in SJF. 1:Halite chevron; 2 Anhedral combined Thenardite,Halite and Bloedite; 3. Bloedite Prismatic- Radial intergrowth; 4. Lenticular gypsum with Eugsterite. (PPL).Length: 6,1 mm

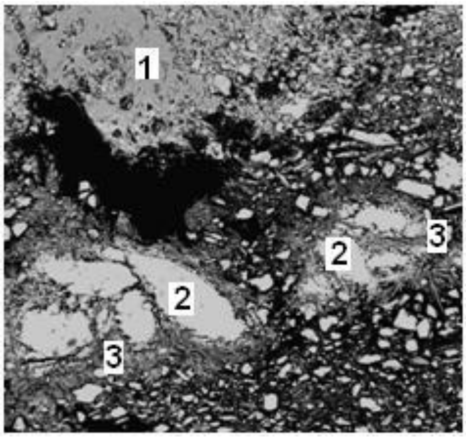

Figure 2. Salt crust in SJF (Detail). 1. Anhedral Bloedite; 2 Corroded lenticular gypsum; 3. Acicular Eugsterite. BSE image . Length: 450 µm

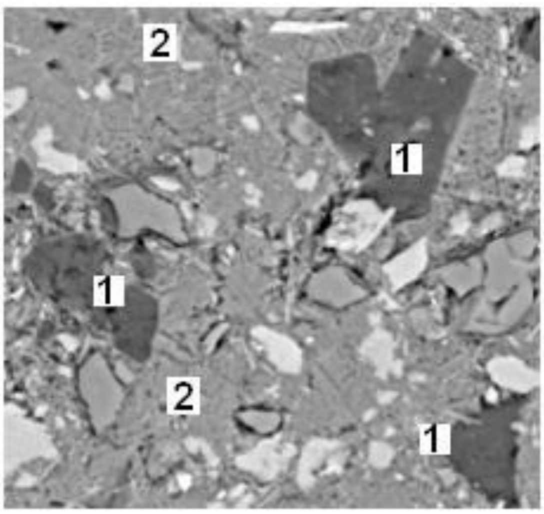

Figure 3. Salt crust of GR 1.Subhedral crystals of Gaylussite; 2 Anhedral mass of Trona. BSE image . Length:240 µm

Figure 4. Nest of Baritocelestite. prismatic crystals into groundmass. BSE image . Length: 240 µm

Calcite is very frequent in the soil of the region. A specific accumulation has been identified in alkaline soils in GR and SLF. This form of calcite is the result of the retrogradation of alkalinity when calcium appears in high proportion in irrigation water (Ribolzi et al. 1973). It has been identified by optical microscopy, XRD and SEM-BSE combined with EDS.

4. Conclusions.

A total of 21 mineral species were identified, some of them previously unknown in the area: Glauberite, Eugsterite, Barite, Baritocelestite, Hexahydrite and Epsomite in non-alkaline salt accumulations, and Thermonatrite, Gaylussite, Norhtupite and Ettringite in alkaline soils.

At a regional scale, three different geochemical facies were recognized with a distribution controlled by the composition of the substrate: a Na-Mg-Cl-SO_4 and a Na-(Mg)-Cl-SO_4 facies related to the presence of geological materials with gypsum, and an alkaline Na-Cl-SO4-CO3 facies associated to fine-grained detritic sediments.

Applying optical microscopy, SEM-SE, SEM-BSE and EDS microanalytical techniques on the same thin section, plus XRD analysis, allows a reliable identification of minerals. The application of SEM-BES techniques is particularly advantageous in the determination of soil constituents (Wierzchos et al. 1995).

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