ALLOPHANE IN WEATHERED ZONES OF BARITE ORE DEPOSITS (VIDE DE ALBA AND SAN BLAS, ZAMORA, SPAIN): MINERALOGY AND GENESIS

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ABSTRACT: The allophane studied occurs in the weathered zones of the barite-sulphide-bearing dolomitic levels, interbedded in the barite ore deposits of Vide de Alba and San Blas (Province of Zamora). These ore deposits are interstratified in the Silurian-Devonian sulphide bearing volcano sedimentary materials of the Alcañices Synform. The allophanic samples have been studied by polarizing microscopy, SEM, XRD, DTA, TG, IRS, EMA and chemical analyses, the last after dissolving the samples by acid (HF + HNO₃ + 3HCl + H₃BO₃) and alkaline digestion (0.5 M NaOH). It is suggested that allophane originates from the reaction of acid solutions released during the weathering of sulphides with acid volcanoclastic rocks. Silica-alumina gels were deposited in holes formed during earlier dissolution of the dolomite associated with the barite ores. Later processes of desilication partially transform allophane to gibbsite.

The allophane studied was detected in the weathered zones of the barite ore deposits of Vide de Alba and San Blas (Province of Zamora), which were studied by Moro (1980), Moro & Arribas (1980), Moro (1981) and Moro et al. (1981).

Allophane occurs in different weathering environments, but it is particularly abundant in soils from tropical to subtropical geographic zones, provided the nature of the bedrock is suitable. Thus, it has been mentioned in tropical areas as a weathering product of basalts and of acid and basic pyroclastic rocks (Sieffermann et al., 1968; Sieffermann & Millot, 1969; Wada et al., 1972; Parfitt & Wilson, 1985; Quantin, 1985). It has also been recorded as a weathering product of volcanic ashes and lapilli under a Mediterranean climate (Quantin et al., 1985), in podzols developed on acid igneous rocks (Newman & Brown, 1987), as weathering products of basalts under an Arctic climate (Evans & Chesworth, 1985), and aluminosilicates in metallic ore deposits (Lukashev, 1958; Callière et al., 1982), and filling fractures in granites (Callière et al., 1982).

The aim of this paper is to show the occurrence, nature and possible genesis of noncrystalline clays, allophane-like material, in weathering zones of the barite ore deposits hosted in sulphide bearing acid volcanoclastic rocks.

LOCATION AND GEOLOGY

The barite ore deposits of Vide de Alba and San Blas are situated on the middle-western zone of the province of Zamora. The Ambiciosa mine is 2 km SW of Vide de Alba, and the
M. Carmen mine is 1 km W of San Bias. Both ore deposits occur in volcano-sedimentary materials, dated as Late Silurian–Early Devonian, from the Alcaníces Synform (Fig. 1).

According to Moro (1980) and Moro & Arribas (1980), the Vide de Alba mine is constituted by a 10–15 m thick lenticular subvertical bed of massive gray barite, with disseminated sulphides. In this bed, barite-sulphide-bearing dolomitic levels are observed. To the top and bottom of this lenticular bed, there are other thinner beds formed by nodular and lenticular barite, vitrinite seams (Poole et al., 1990) and finely banded sulphides and sulphosalts, among which pyrite, tetrahedrite, sphalerite and chalcopyrite are of note. In these latter beds, barite is finely interlayered with siliceous, siliceous-sericitic and carbonated seams. Underlying the ore deposits, the host rocks are constituted by feldspatic quartzites and an alternation of lidites, amapelites, sulphide bearing acid

Fig. 1. Geological map of the NW of Zamora province, where the barite mines are located. 1, Vide de Alba and 2, San Bias ore deposits.
volcanoclastic rocks and quartzitic breccia. Chert, volcanic ashes, thin stratified lidites and schists, graywackes and sandstones overlie this ore deposit (Fig. 2A).

The San Blas ore deposit is quite similar but the beds of massive barite have a variable thickness between 10 cm and 1 m, and they alternate with siliceous, carbonate and schistose levels, with varying amounts of barite. As in the Vide de Alba ore deposit, the host rocks are constituted at the bottom, by alternating beds of feldspathic quartzites, lidites, ampellites and volcanic ashes, and fanglomerates, schists, quartzites and graywackes. Overlying the ore deposit, there are schists, quartzites and graywackes (Fig. 2B).

According to Moro (1980) and Moro & Arribas (1980), these ore deposits have a volcanosedimentary origin, having recrystallized later by diagenetic and metamorphic processes.
RESULTS

Characteristics of the samples

The samples are from the weathered and unaltered barite-sulphide-bearing dolomitic levels of the ore deposits. The allophanic samples have a spongy structure and the barite crystals are cemented by a vitreous and translucid material (allophane) with a bluish colour resembling that of celestine (Fig. 3). This material is usually mixed with another with a milky colour and an earthy appearance. Depending on the content of Fe oxyhydroxides, the colour changes from bluish or white to red ochre.

The unaltered samples are massive, beige, with marble appearance, and heterogranular and granoblastic texture. The barite crystals are xenomorphic to idiomorphic and usually appear in tabular and radial aggregates. These samples are constituted by dolomite, magnesian calcite and barite as essential minerals, and by quartz, sericite, pyrite, sphalerite and tetrahedrite as accessory phases (Fig. 4).

Polarizing and scanning electron microscopy (PM & SEM)

By PM, the allophane has a collophorm texture and is isotropic, and occasionally contains spots of Fe oxyhydroxides with a more or less well developed collophorm texture. In addition, traces of quartz and phyllosilicates have been observed (Fig. 5). An electron image (Fig. 6) at low magnification (× 145) shows the massive and gel-like aspect of the allophane, as well as the conchoidal fractures and the shrinkage cracks due to dehydration under the vacuum in the microscope. The distribution of Ba in an allophanic sample overlapped on the electron image is shown in Fig. 7a while Fig. 7b shows the distribution of Si and Al.

X-ray diffraction (XRD)

The XRD patterns of the bulk sample, <2 µm fraction and an allophanic concentrate are shown in Fig. 8. The <2 µm fraction was separated by sedimentation techniques after
dispersion of the bulk sample at pH = 8.2; the allophanic concentrate was obtained by hand picking under a binocular lens.

In all X-ray patterns barite is the major phase accompanied by minor gibbsite (4.83, 2.39, 2.16 and 1.81 Å).

In the XRD pattern of the <2 μm fraction, a reflection at 7.37 Å is due to halloysite and two others at 4.18 and 2.56 Å are due to goethite.

The background line in the X-ray patterns corresponding to the <2 μm fraction and to the allophanic concentrate show two diffraction bands between 4.39 and 3.09 Å, and 2.56 and 2 Å, with maxima centred at 3.3 and 2.26 Å; these approximately coincide with those described by White (1953) and Yoshinaga & Aomine (1962a) for allophanes.
Fig. 6. Secondary electron image of the allophane. Notice the conchoidal fracture and the shrinkage cracks.

Fig. 7. Electron image of the barite cemented by allophane (backscattered electrons). a: Al and Si mapping overlapped on the barite image; barite in white, allophane in black. b: Idem to the former, with the Ba mapping. Barite in black; allophane in light grey.

**Differential thermal and thermogravimetric analyses (DTA and TG)**

On the DTA curve of the <2 μm fraction (Fig. 9a), the first endothermic effect, at 102°C, has been assigned to loss of moisture. The second endotherm, at 280–300°C, could correspond to the dehydroxylation of some Al(OH)₃ polymorphs, bayerite or gibbsite. However, as gibbsite was the phase identified by XRD, this second effect corresponds to the
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**FIG. 8.** XRD patterns of the three fractions studied (powder method).
following transformation: $\gamma\text{Al(OH)}_3 + \Delta T^\circ C \rightarrow \chi\text{Al}_2\text{O}_3$. The difference between the observed temperature and the one given by Mackenzie (1970), 30-50°C, can be explained by the presence of Fe in the gibbsite structure, or to the equipment. On the other hand, goethite is transformed to hematite in the temperature range 190–380°C, depending on the particle size (Mackenzie, 1970). Consequently, it could be assumed that in this second effect the transformation of goethite could also be concealed by the dehydroxylation of gibbsite.

The third endothermic effect, at 483°C, could be due to the transformation of alumina gels such as “pseudoboehmite” (Mackenzie, 1970) to $\gamma\text{Al}_2\text{O}_3$. However, due to the breadth of the peak it could be assumed that the endothermic effect due to halloysite is concealed by the dehydroxylation of alumina gels.

The exothermic effect at 891°C has been assigned to the transformation $\gamma\text{Al}_2\text{O}_3 + \Delta T^\circ C \rightarrow \theta/\delta \text{Al}_2\text{O}_3$; this takes place between 850 and 930°C (Mackenzie, 1970).

Barite is inert in the temperature range covered (up to 1000°C approximately).

The DTA pattern of the allophanic concentrate (Fig. 9c) is characteristic of this mineraloid, with an accentuated endothermic effect at 140°C and another sharp exothermic effect at 985°C. The former is due to loss of moisture, and the latter to the transformation of allophane to Al spinel (Smykatz-Kloss, 1974), or mullite and/or $\gamma\text{Al}_2\text{O}_3$ (Tsuzuki & Nagasawa, 1960; Yoshinaga & Aomine, 1962a,b). There are also two endothermic inflections, at 285-300°C and 470-500°C suggesting the presence of traces of gibbsite, and “pseudoboehmite” and/or halloysite. On the other hand, the TG curve (Fig. 9d), shows a rapid loss of weight up to 140°C, and a more gradual loss between 140 and 450°C. The shape

Fig. 9. DTA and TG patterns of the <2 $\mu$m fraction and the allophanic concentrate, composed of allophane plus barite.
of the first part of the curve is due to loss of moisture, ~12%, while the shape of the second part is possibly due to the loss of OH− groups bonded to Si and Al. The energy of these bonds would be variable, because the slope of the TG curve is constant between 140 and 450°C, and no endothermic effect is observed on the DTA curve as occurs for imogolite (Wada, 1977).

**Infrared (IR) spectroscopy**

Because of the difficulty in separating pure allophane, IR spectra were obtained from the pure barite and the allophanic concentrate composed of barite plus allophane (Fig. 10). Both sample were dried at 110°C for 24 h, mixed with KBr and compressed to obtain pellets.

In spectrum A, three regions of maximum absorption, ν3, ν4 and ν1, can be distinguished, corresponding to the internal vibrations of SO4^2− groups. In ν3, there are three maxima at 1190, 1130 and 1080 cm\(^{-1}\), whereas in ν4 there are two at 640 and 620 cm\(^{-1}\). The sharp absorption maximum at 980 cm\(^{-1}\) has been assigned, according to Rull *et al.*, (1989), to the region of vibration ν1. These authors analysed several celestines by IR and obtained similar spectra to that for the barite studied, at least in the range of internal frequencies of the SO4^2− groups.

In spectrum B, corresponding to allophane plus barite, the first absorption region, with a maximum at 3525 cm\(^{-1}\), is usually assigned to the OH-stretching vibrations of either adsorbed water or structural OH groups of allophane. As the specimens had been dried at 110°C for 24 h, this first maximum could be due to the water released, according to the TG curve, in the range 140–450°C. The second maximum, at 1650 cm\(^{-1}\), is due to the HOH deformation vibrations. The peaks at 980 and 600 cm\(^{-1}\), respectively, are mainly attributed to Si(Al)O stretching vibrations, and partially to SiOH and AlOH deformation vibrations (Wada, 1977); in these two regions there is an overlap of the internal vibrations of the SO4^2− groups of the barite.

**Chemical analyses**

Table 1 shows the semi-quantitative chemical analyses of allophane, obtained using a Camebax-SX50 electron microprobe. According to these data, the allophane studied shows Si : Al ratios ranging between 0.83 and 0.94 corresponding to an Si-rich allophane composition, according to Parfitt's (1990) classification.

The <2 μm fraction and allophanic concentrate have been analysed after dissolution by acid (HF + HNO3 + 3HCl + H3BO3) and alkaline digestion, the latter, using 0.5 M NaOH according to Hashimoto & Jackson (1960). In the acid solutions, all determinations were carried out by ICP spectroscopy except Na2O and K2O which were obtained by AA spectroscopy. In the alkaline solutions, SiO2 and P2O5 were also determined by ICP, and Al2O3 by AA. The insoluble residue from both fractions was determined by gravimetry, after ignition at 950°C for 2 h.

In the <2 μm fraction, organic and mineral CO2 were determined using a Leco CS-244 elemental analyser, and F− by a selective ion electrode; H2O\(_\text{T}\) was determined by gravimetry, after ignition at 950°C of 2 h. Thus, decomposition of barite was avoided as much as possible.

The calcination loss of the allophanic concentrate was obtained from the DTA curve. The results obtained from the four solutions are shown in Tables 2 and 3. The Si : Al ratio of the
soluble phase by acid digestion of the allophanic concentrate is 1:1, which is approximately in agreement with the semi-quantitative results obtained by electron microprobe.

The mineralogical distribution of the major elements (Si, Al, Fe, S and Ba) in the two
Oxides %  

<table>
<thead>
<tr>
<th>Oxides</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>(\bar{x})</th>
<th>(\sigma)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO(_2)</td>
<td>46.91</td>
<td>45.51</td>
<td>41.26</td>
<td>42.45</td>
<td>44.03</td>
<td>2.27</td>
</tr>
<tr>
<td>Al(_2)O(_3)</td>
<td>43.35</td>
<td>41.81</td>
<td>42.28</td>
<td>42.11</td>
<td>42.39</td>
<td>0.58</td>
</tr>
<tr>
<td>CaO</td>
<td>0.15</td>
<td>0.14</td>
<td>0.28</td>
<td>0.15</td>
<td>0.18</td>
<td>0.06</td>
</tr>
<tr>
<td>CuO</td>
<td>0.00</td>
<td>0.00</td>
<td>0.93</td>
<td>0.72</td>
<td>0.41</td>
<td>0.41</td>
</tr>
<tr>
<td>BaO</td>
<td>0.04</td>
<td>0.00</td>
<td>0.06</td>
<td>0.04</td>
<td>0.03</td>
<td>0.02</td>
</tr>
<tr>
<td>P(_2)O(_5)</td>
<td>0.03</td>
<td>0.09</td>
<td>0.14</td>
<td>0.05</td>
<td>0.08</td>
<td>0.04</td>
</tr>
<tr>
<td>NaO</td>
<td>0.09</td>
<td>0.05</td>
<td>0.00</td>
<td>0.00</td>
<td>0.04</td>
<td>0.04</td>
</tr>
<tr>
<td>K(_2)O</td>
<td>0.31</td>
<td>0.34</td>
<td>0.49</td>
<td>0.26</td>
<td>0.35</td>
<td>0.09</td>
</tr>
<tr>
<td>MgO</td>
<td>0.02</td>
<td>0.03</td>
<td>0.00</td>
<td>0.00</td>
<td>0.01</td>
<td>0.01</td>
</tr>
<tr>
<td>FeO</td>
<td>0.13</td>
<td>0.15</td>
<td>0.42</td>
<td>0.24</td>
<td>0.24</td>
<td>0.11</td>
</tr>
<tr>
<td>MnO</td>
<td>0.39</td>
<td>0.44</td>
<td>0.00</td>
<td>0.00</td>
<td>0.21</td>
<td>0.21</td>
</tr>
<tr>
<td>ZnO</td>
<td>0.00</td>
<td>0.00</td>
<td>0.13</td>
<td>0.00</td>
<td>0.03</td>
<td>0.05</td>
</tr>
<tr>
<td>Sb(_2)O(_5)</td>
<td>0.00</td>
<td>0.00</td>
<td>0.11</td>
<td>0.04</td>
<td>0.04</td>
<td>0.04</td>
</tr>
<tr>
<td>Total</td>
<td>91.42</td>
<td>88.56</td>
<td>86.10</td>
<td>86.06</td>
<td>88.04</td>
<td>2.20</td>
</tr>
<tr>
<td>SiO(_2)/Al(_2)O(_3)(*</td>
<td>1.81</td>
<td>1.85</td>
<td>1.68</td>
<td>1.73</td>
<td>1.77</td>
<td>0.07</td>
</tr>
<tr>
<td>%SiO(_2)/%Al(_2)O(_3)</td>
<td>1.08</td>
<td>1.09</td>
<td>0.98</td>
<td>1.01</td>
<td>1.04</td>
<td>0.05</td>
</tr>
<tr>
<td>Si/Al(**)</td>
<td>0.92</td>
<td>0.93</td>
<td>0.83</td>
<td>0.94</td>
<td>0.91</td>
<td>0.04</td>
</tr>
</tbody>
</table>

A, B, C and D: analysed spots. (*) Molar ratio. (**) Atomic ratio

fractions studied is summarized in Table 4. This distribution is based on the data shown in Tables 1 to 3, taking into account that the average molar ratio SiO\(_2\)/Al\(_2\)O\(_3\) of the allophane is 1.77, as obtained by electron microprobe.

In the <2 \(\mu\)m fraction, the difference between the Al\(_2\)O\(_3\) of the acid and alkaline solutions, 8.48%, is due to the non quantitative extraction of free Al hydroxides and/or to the existence of insoluble phyllosilicates by the alkaline digestion carried out. The Fe\(_2\)O\(_3\) occurs principally as goethite and originates from oxidation of pyrite. The P\(_2\)O\(_5\) is mainly adsorbed by allophane which can adsorb up to 10% P\(_2\)O\(_5\) (White, 1953; Chukhrov et al., 1965); P is abnormally high in the Devonian-Silurian materials form the Alcafiaces Synform. Organic CO\(_2\) can be due to humic and/or fulvic acids which are stabilized as an organometallic complex with Si-Al gels as in Andosols (Parfitt, 1990). Copper, which is responsible for the bluish colour of the allophane, and Zn, Sb and Ni originate from oxidation of sulphides and sulphosalts associated with barite. Barium and Sr come from barite and are all mostly adsorbed by allophane; the same applies to Ca, Mg, Na, K and Mn.

**GENESIS**

According to Wada (1977), the most important factors that determine the formation of allophane in soils are: (1) Bedrock composed of acid or basic igneous rocks, especially of pyroclastic origin. (2) A tropical or subtropical climate; although this is not a necessary condition, it favours allophane formation. (3) Well drained and leached soils, with pH between 5 and 7. (4) SiO\(_2\) concentration in soil solution of 20 p.p.m or, according to Parfitt & Wilson (1985), 15 p.p.m; these concentrations are controlled by rainfall, the drainage of the soil and the seasonal character of the climate. (5) High Al activity in the soil solution favours the formation of allophane and imogolite. (6) The presence of important amounts
of humic and fulvic acids prevents the formation of allophane and favours that of opal, due to chelation of Al.

Due to its amorphous or slightly structured character, allophane and imogolite are metastable phases, and therefore are the transition products in the alteration of primary minerals and amorphous volcanic materials to secondary minerals. Thus, their residence time in the soil is short, approximately 5000–10000 years (Wada, 1977). However,
Allophane in weathered barite deposits

Table 3. Chemical composition of the soluble phases by alkaline digestion (Hashimoto & Jackson, 1960)

<table>
<thead>
<tr>
<th>Oxides</th>
<th>&lt;2 μm fraction</th>
<th>Allophanic concentrate</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>5.34</td>
<td>14-59</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>8.82</td>
<td>16-17</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>0.61</td>
<td>0.63</td>
</tr>
<tr>
<td>I.R.</td>
<td>67.37</td>
<td>46-53</td>
</tr>
<tr>
<td>L.W.</td>
<td>16-79(1)</td>
<td>21-67(2)</td>
</tr>
</tbody>
</table>

I.R. = insoluble residue. L.W. = loss of weight:
(1) ignited at 950°C for 2 h.
(2) by TGA.

Table 4. Mineralogical distribution of major elements (Si, Al, Fe, S and Ba)

<table>
<thead>
<tr>
<th>Minerals</th>
<th>&lt;2 μm fraction</th>
<th>Allophanic concentrate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Allophane</td>
<td>5.34% SiO₂ + 5.14% Al₂O₃</td>
<td>14-59% SiO₂ + 14.03% Al₂O₃</td>
</tr>
<tr>
<td>Gibbsite + Al-gels</td>
<td>3.68% Al₂O₃ + (X × 8-48%)Al₂O₃</td>
<td>2.14% Al₂O₃</td>
</tr>
<tr>
<td>Phyllosilicates + quartz</td>
<td>8.48% - (X × 8-48%)Al₂O₃ + 4-46% SiO₂</td>
<td>1.1% Al₂O₃ + 5.74% SiO₂</td>
</tr>
<tr>
<td>Goethite</td>
<td>~7-0%</td>
<td>~</td>
</tr>
<tr>
<td>Barite</td>
<td>47.16%</td>
<td>38.8%</td>
</tr>
</tbody>
</table>

X = unknown factor, <1.

Stevens & Vucetich (1985) suggested that allophane can remain in tephra beds for at least 250,000 years in rainfall areas of New Zealand. Allophane is transformed to halloysite by resilication, and to gibbsite by desilication, processes also closely related to the climatology and the drainage of the soil (Wada, 1977).

Although in our samples allophane is not directly related to soils developed on pyroclastic rocks, these materials do constitute the host rock of the barite ore deposits. For this reason, it is assumed that the pyroclastic rocks, upon alteration under acidic conditions due to the supergenic oxidation of sulphides, are the source of the necessary Al and Si for the formation of allophane.

When the textures of the altered and unaltered samples with allophane are compared, it can be deduced that this gel was formed by precipitation in the holes formed during previous dissolution of the dolomite associated with barite. This dissolution process was enhanced by the low pH of the waters from the oxidation of the sulphides and sulphosalts. In turn, this low pH favoured the later formation of allophane.

The drainage and leaching are due to the intense fracturing which affects the barite ore deposit. The content of alkaline, alkaline-earth cations and anions of the samples studied is extremely low, and these elements do not form discrete minerals.

Due to the short life of allophane, the formation process of the gel studied can be considered as a recent phenomenon, and originated under climatic conditions similar to those at present, though probably more humid.

Finally, there are significant amounts of gibbsite, heterogenously distributed at the scale of the sample. This fact suggests that once the allophane was formed, a heterogeneously distributed desilication process was produced and is still ongoing. This process can be
related to a lowering of the water table, which would improve the drainage of the most superficial level. Halloysite could have originated at the same time as allophane or formed from it by resiliication, during periods of stagnant moisture.

**ACKNOWLEDGMENTS**

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