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Ni, Mn, Zn,Cr - SMECTITES, EARLY AND EFFECTIVE TRAPS FOR TRANSITION ELEMENTS IN SUPERGENE ORE DEPOSITS.

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ABSTRACT

Ni, Mn, Zn, Cr - rich smectites were identified as early authigenic minerals in the weathered products of metalliferous ultramafic rocks from Brazil and Ivory Coast and in the weathered material of a sulfidic (Cu - Pb - Zn) deposit from Congo. In the case of the divalent transition metals, these are trioctahedral smectites. In the case of Cr which is trivalent under weathering conditions, the authigenic smectites are dioctahedral. Trioctahedral smectites are unstable, as environment undergoes lixiviation. In the general case, there is a transition from the Ni, Mn, Zn - rich trioctahedral to dioctahedral smectites, with progressive leaching of Mg, Ni, Mn, and Zn and enrichment in Al and above all in Fe. The final term of weathering consists of the formation of kaolinites and of oxi-hydroxides whose lattice traps in its turn the transition metals, released by destruction of the smectitic lattices. Thus, at the beginning of weathering, these transition metals have a lithophilic behaviour, whereas at the final term of weathering, they have a siderophilic one .

INTRODUCTION

Ni, Mn, Zn-rich smectites were identified as authigenic clay minerals in profiles developped from ultramafic rocks of Ivory-Coast(Colin et al., 1980; Paquet et al., 1981; Nahon et al., 1982 a and b; Paquet et al.,1983) and of Brazil(Melfi et al., 1980; Boukili, 1984; Boukili et al., 1984; Colin, 1984; Colin et al., 1985),as well as in the weathered products of a Cu, Pb, Zn-bearing sulfidic ore deposit of Congo(Koud, 1985).

Ni-rich smectites were subject to more detailed studies than manganiferous, chromian and Zn-bearing ones. Thus, they will serve as model.

1. Ni - RICH SMECTITES

These nickeliferous smectites were found by Colin (1984) in the Archean ultramafic district of Niquelandia, Brazil. The pit of Jacuba shows a lateritic profile which was derived from pyroxenites enclosed in a dunitic massif; the smectitic weathering levels are about 15 meters thick.

1.1. In the lower weathering level (coarse saprolite), the clay plasma was formed by interaction between pyroxenes (enstatite and diopside) and lixiviation solutions from dunites. This plasma is essentially composed of smectites characterized by their usual honeycomb habitus (Fig.1, 2).

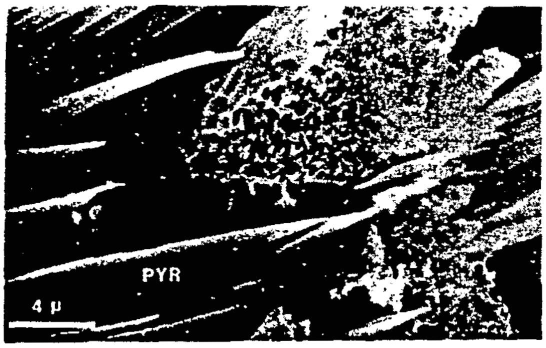

Figure 1. Incipient formation of smectite with honeycomb habitus from a pyroxene, Profile of Jacuba, Brazil (Colin, 1984).

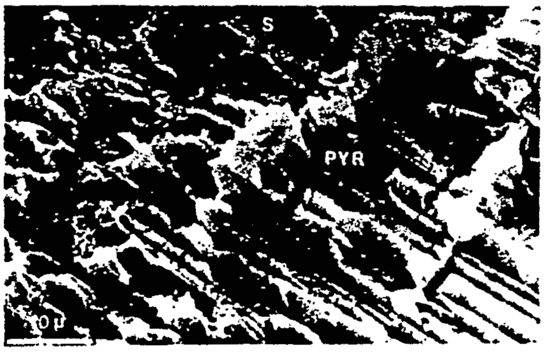

Figure 2. Development of smectitization from cleavages of pyroxene, Profile of Jacuba, Brazil (Colin, 1984).

Microprobe analyses were carried out in greenish areas of the plasma. These analyses are plotted on Fig.3 and correspond to two groups of smectites.

(a) A group of Ni-rich saponites in the areas close to the original pyroxene crystals, which are called "Plasma 1 smectites" on Fig.3. The average structural formula is the following :

$$[Si_{3.67}\ Al_{0.325}\ Fe_{0.005}]\ [Ni_{2.14}\ Al_{0.10}\ Fe^{3+}_{0.35}\ Mg_{0.12}\ Ti_{0.009}\ Cr^{3+}_{0.09}\ Cu^{2+}_{0.03}]$$

$$O_{10}\ (OH)_2\ Ca_{0.01}\ K_{0.05}$$

$$NiO = 31\ \% \qquad \Sigma_{oct.} = 2.81$$

In this group of smectites, octahedral Ni ranges between 1.68 to 2.74.

(b) A group of Ni, Fe saponites in the external areas of the plasma, which are called "Plasma 2 smectites" on Fig.3. Their average structural formula is the following :

$$[Si_{3.66}\ Al_{0.335}\ Fe_{0.005}]\ [Ni_{1.26}\ Al_{0.346}\ Fe^{3+}_{0.54}\ Mg_{0.17}\ Cr^{3+}_{0.175}\ Ti_{0.013}\ Cu^{2+}_{0.046}]\ O_{10}\ (OH)_2\ Ca_{0.036}\ K_{0.065}$$

$$\Sigma_{oct.} = 2.49 \qquad NiO = 19\ \%$$

In this group, octahedral Ni ranges between 0.85 and 1.76.

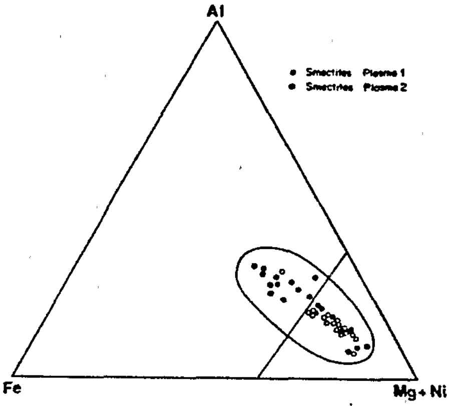

Figure 3. Smectites from the lower weathering level (coarse saprolite), Profile of Jacuba, Brazil (after Colin, 1984).

1.2. In the upper weathering level (fine saprolite), the greenish-yellow plasma is generated by the external part of the smectitic plasma from the underlying weathering level, described above. The greenish-yellow plasma is principally made of smectites along with low content of kaolinite.

Smectites analyzed by microprobe are distributed in three groups, as showed on Fig.4 :

- Ni, Fe, saponites,
- Ni - rich hisingerites which are considered as transitional between trioctahedral and dioctahedral smectites according to Brigatti (1981),
- Fe, Ni beidellites which are dioctahedral smectites.

Smectites called "Plasma 3 smectites" correspond to the internal areas and smectites called "Plasma 4 smectites" to the external areas of the greenish-yellow plasma. The average structural formulas are the following :

(a) For Ni, Fe saponites

$$[Si_{3.767}\ Al_{0.233}]\ [Ni_{0.902}\ Al_{0.485}\ Fe^{3+}_{0.725}\ Mg_{0.179}\ Cr^{3+}_{0.098}]\ O_{10}\ (OH)_2\ Ca_{0.020}\ K_{0.059}$$

$$\Sigma_{oct.} = 2.38 \qquad NiO = 14\ \%$$

In this group, octahedral Ni ranges from 0.80 to 1.10.

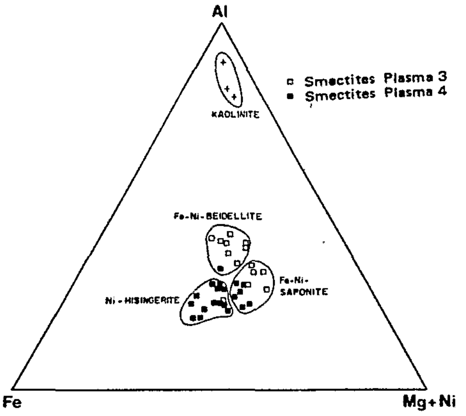

Figure 4. Smectites from the upper level (fine saprolite), Profile of Jacuba, Brazil (after Colin, 1984).

(b) For Ni-rich hisingerites

$$[Si_{3.634}\ Al_{0.351}\ Fe_{0.015}]\ [Ni_{0.737}\ Al_{0.290}\ Fe_{1.015}\ Mg_{0.242}\ Ti_{0.007}\ Cr_{0.117}\ Cu_{0.02}]\ O_{10}\ (OH)_2\ Ca_{0.027}\ K_{0.056}$$

$$\Sigma_{oct.} = 2.40 \qquad NiO = 11.3\ \%$$

Octahedral Ni ranges between 0.51 and 1.03.

(c) For Fe, Ni beidellites

$$[Si_{3.684}\ Al_{0.316}]\ [Ni_{0.623}\ Al_{0.643}\ Mg_{0.24}\ Ti_{0.016}\ Cr^{3+}_{0.178}\ Cu^{2+}_{0.001}]\ O_{10}\ (OH)_2\ Ca_{0.014}\ K_{0.024}$$

$$\Sigma_{oct.} = 2.35 \qquad NiO = 9.7\ \%$$

Octahedral Ni ranges between 0.46 and 0.93.

1.3. In summary, the weathering of ultramafic rocks from Jacuba, Brazil begins with authigenesis of trioctahedral smectites. These trioctahedral smectites have an average content of 2.13 out of 3 octahedral ions per half-unit cell : these are Ni-rich saponites.

As weathering increases, the trioctahedral smectites will change into dioctahedral smectites, in which octahedral Ni only represents up to 0.9 in the octahedral layer.

The final stage of weathering consists of the formation of kaolinites and Ni-goethite. All of the weathering stages from parental minerals to goethite are represented on Fig. 5

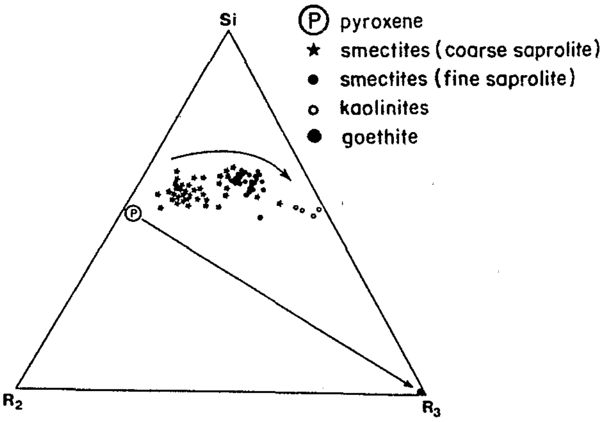

Figure 5. Variations in the chemical composition of the different products generated during weathering, Profile of Jacuba, Brazil (Colin, 1984).

2. Mn-RICH SMECTITES.

These smectites were discovered by Nahon et al.(1982) as early authigenic minerals during the weathering of tephroite, a Mn nesosilicate (Mn_2 SiO_4), in a lateritic profile derived from serpentinized dunites associated with gondites in Ivory-Coast.

Tephroite crystals generated a clay plasma filling corrosion vugs on the surface crystals and cracks. This plasma is essentially composed of smectites which were analyzed by microprobe. The average structural formula is the following :

$$[Si_{3.92}\ Al_{0.8}]\ [Mn^{2+}_{2.37}\ Al_{0.20}\ Fe^{3+}_{0.04}\ Mg_{0.30}\ Cr^{3+}_{0.007}]\ O_{10}\ (OH)_2\ Ca_{0.05}$$

$$\Sigma_{oct.} = 2.91$$

Octahedral Mn ranges between 2.26 and 2.55, which characterizes a Mn-rich trioctahedral smectite.

Nahon et al. (1982) noted that in the upper part of the lateritic profile, smectites disappear and are replaced by an opaque plasma of Mn-oxihydroxides, especially manganite (MnO.OH).

3. Zn-RICH SMECTITES

The weathered products of willemite, a Zn nesosilicate (Zn_2 SiO_4), were studied by Koud (1985) in a mineralized copper, lead, zinc-bearing bed developped from the sandstones-schists formations of Niari, in Congo. Willemite appears as accessory mineral in the Pb-Cu-Zn deposit.

Microprobe analyses were carried out in three points of the clay plasma generated by willemite.From the innermost part (1) to the outermost part (3) of the plasma, the corresponding structural formulas are the following :

(1) $$[Si_{3.24}\ Al_{0.76}]\ [Zn_{2.11}\ Al_{0.60}\ Mg_{0.26}\ Fe_{0.06}]\ O_{10}\ (OH)_2\ K_{0.09}\ Na_{0.02}$$

$$\Sigma_{oct.} = 3.0$$

(2) $$[Si_{3.61}\ Al_{0.39}]\ [Zn_{2.06}\ Al_{0.45}\ Mg_{0.36}\ Fe_{0.06}\ Pb_{0.01}]\ O_{10}\ (OH)_2\ K_{0.04}\ Na_{0.03}$$

$$\Sigma_{oct.} = 2.93$$

(3) $$[Si_{3.66}\ Al_{0.34}]\ [Zn_{1.60}\ Al_{0.90}\ Mg_{0.15}\ Fe_{0.05}\ Pb_{0.01}]\ O_{10}\ (OH)_2\ K_{0.02}\ Na_{0.01}$$

$$\Sigma_{oct.} = 2.70$$

According to the definition of Ross (1946), the smectites analyzed are sauconites, i.e. Zn-rich trioctahedral smectites; in their octahedral layer, Zn is the prevailing cation, ranging between 1,50 and 2.90 per half-unit cell.

Thissmectitic step is only transitional during the weathering of willemite, whose final stage is the formation of zincite (Zn O).

4. Cr-RICH SMECTITES

Cr-rich smectites were identified by Boukili (1984) and Boukili et al. (1984) in the weathering zone of lateritic profiles derived from chromiferous ultramafic rocks from Campo Formoso; Brazil. Before undergoing weathering, these ultramafic rocks were subject to three successive phases of hydrothermal alteration.

As emphasizedby the authors, the chemical composition of the smectites analyzed strongly depends on the nature of parental minerals. These minerals which were formed by hydrothermal alteration are Cr-rich chlorites and Cr hydroxi-carbonates called stichtites. But in both cases, the smectites are Cr-rich, as already noticed by Besnus et al.(1975).

These chromian smectites were analyzed by microprobe and the analyses lead to the following average structural formulas :

4.1. For smectites generated by weathering of stichtite

$$[Si_{3.86}\,Al_{0.14}]\,[Cr^{3+}_{0.86}\,Al_{0.13}\,Fe^{3+}_{0.27}\,Mg_{0.93}\,Ni_{0.07}]\,O_{10}\,(OH)_2$$

$$\Sigma_{oct.} = 2.26$$

in which octahedral Cr ranges from 0.74 to 0.98 out of 2 ions per half-unit cell.

After the definition of Brindley and Brown(1980), this formula corresponds to volkonskoite, a dioctahedral smectite with prevailing Cr cation in the octahedral layer.

4.2. For smectites generated by weathering of Cr-chlorites

$$[Si_{3.69}\,Al_{0.31}]\,[Al_{0.31}\,Fe^{3+}_{1.02}\,Mg_{0.37}\,Cr^{3+}_{0.26}\,Ni_{0.1}]\,O_{10}\,(OH)_2$$

$$\Sigma_{oct.} = 2.06$$

in which octahedral Cr ranges between 0.23 and 0.48 out of 2 ions per half-unit cell.

This formula corresponds to a chromian nontronite, which is also a dioctahedral smectite.

4.3. The early stage of weathering of chromian minerals formed by hydrothermal alteration consists of an authigenesis of smectites which trap Cr. These smectites are Cr-rich dioctahedral smectites and belong to the group of volkonskoites and to the series of chromian beidellites-nontronites.

As weathering increases, the environement becomes more open, and smectites are replaced by a mineral association of kaolinite and Cr-goethite (up to 4% Cr_2O_3).

5. TRIOCTAHEDRAL SMECTITES : A STAGE OF THE WEATHERING ULTRAMAFIC ROCKS WITH ACCUMULATION OF TRANSITION METALS.

5.1. The role of trioctahedral smectites as the first step of magnesian silicates weathering is confirmed. The study of peridotites from Ivory-Coast showed (Colin et al., 1980; Paquet et al.,1981; Nahon et al.,1982)that the alteration products in the core of altered olivine and pyroxene crystals are trioctahedral Mg-smectites (stevensites, saponites).

Then, chemical analyses of isolated particles populations representing progressive weathering stages of peridotites was carried out by dispersive energy spectrometry (Paquet et al. 1983). This technique demonstrated that chemical compositions vary inside each mineral sample population.Moreover, a statistical shift of successive particles during increasing weathering was noted, with transition from trioctahedral to clearly dioctahedral smectites such as nontronites, through a series of Mg-Fe transition terms (Fig.6). This means that the stronger the lixiviation, the more Mg is released.

The present study confirms that during weathering of ultramafic rocks authigenic trioctahedral smectites can be Ni, Mn, Zn-rich, such as Ni-saponite, Mn-saponite and Zn-saponite (sauconite), depending on the chemical composition of the parent mineral.

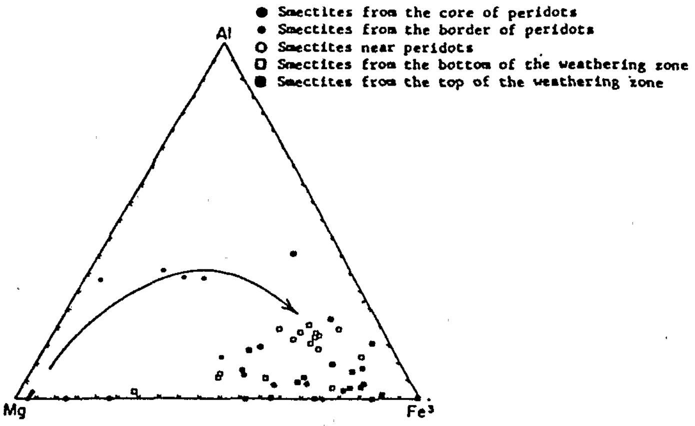

Figure 6. Variations in the chemical composition of isolated particles of smectites,Profile of Biankouma,Ivory-Coast.

5.2. Ni-rich trioctahedral smectites. The study of the weathering of Ni-bearing peridotites already indicated the formation of nickeliferous trioctahedral phyllosilicates of the serpentines and talcs groups (Trescases, 1973, 1979; Besset, 1978; Melfi et al., 1980; Colin et al.,1980; Paquet et al., 1981). The study of supergene alteration of ultramafic rocks from Brazil (Colin, 1984; Colin et al., 1985) pointed out clearly that another stage exists during which Ni is abundantly trapped in octahedral layers of saponites. Ni ions may represent more than 2 octahedral ions out of 3 per half - unit cell. Mg and Ni contents decrease with increasing weathering, whereas Al and above all Fe contents increase,resulting in dioctahedral smectites, such as Fe, Ni beidellites and nontronites. Last, kaolinites and above all Ni-goethite form.

5.3. Mn and Zn-rich trioctahedral smectites. Similarly, the weathering of two nesosilicates, tephroite (Mn_2SiO_4) from Ivory-Coast and willemite (Zn_2SiO_4) from Congo leads to trioctahedral smectites as first weathering stage : Mn saponites and Zn saponites (sauconites) with more than 2 octahedral Mn or Zn ions per half-unit cell. As weathering increases, Mn^{2+} and Zn contents decrease, like Mg, and nontronites first and Mn or Zn oxides later form.

5.4. Chromian dioctahedral smectites. The case of chromium is different from that of the three other divalent Ni, Mn and Zn transition metals. Cr is above all trivalent under weathering conditions similarly to Fe and Al.This is why Cr-rich dioctahedral smectites are observed. The Cr content can reach 0.75 to 1 octahedral ion out of 2 per half-unit cell, which defines volkonskoite. Increasing weathering leads to chromian beidellites and nontronites, then to kaolinites and Cr-oxides.

6. CONCLUSIONS.

- Ni, Mn, Zn-rich trioctahedral smectites can form similarly to magnesian ones, i.e. as early authigenic clay minerals during weathering of silicates rich in these divalent transition metals.
- These trioctahedral smectites are unstable, in an environment undergoing lixiviation. The divalent transition metals such as Ni, Mn and Zn are progressively lixiviated along with Mg. In the general case, there is a transition from the Ni, Mn, Zn-rich trioctahedral to dioctahedral smectites which are progressively impoverished in Mg, Ni, Mn, Zn and enriched in Al and above all in Fe. The next stage will consist of the formation of kaolinites and Fe (Ni), Mn and Zn oxi-hydroxides. Chromium, which is trivalent directly enters dioctahedral smectites which are progressively

replaced by kaolinite and Cr-goethite.

- Transition from the lithophilic behaviour to the siderophilic one is to be emphasized. In fact, the divalent Ni, Mn and Zn and the trivalent Cr transition metals accompany Mg, Fe and Al in secondary silicates during a first weathering stage. This is a lithophilic behaviour. At the end of weathering, Si and Al form kaolinites, whereas the transition metals are released and recombined as oxi-hydroxides, such as goethite, Ni-goethite, manganite, zincite and Cr-goethite. This is a siderophilic behaviour.

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