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DEHYDRATION OF AMMONIUM TRIOXALATOCHROMATE(III) AND TRIOXALATOFERRATE(III) IN RELATION WITH THE PREPARATION OF METALLIC MIXED-OXIDES.

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ABSTRACT

The different steps appearing during the dehydration processes of ammonium trioxalatochromate(III) and ferrate(III) have been investigated by considering 1) - their crystallization diagrams, 2) - thermogravimetry (TG) under controlled water pressure and 3) - differential thermal analysis (DTA). In the case of ammonium trioxalatoferrate(III) trihydrate $(NH_4)_3[Fe(C_2O_4)_3].3H_2O$ the TG curves exhibit a plateau corresponding to the dihydrate intermediate. For the chromate(III) the dehydration equilibrium is divariant. These observations are discussed in terms of the crystal structures of both investigated solids, especially on the basis of the specific role played by one of the three water molecules in the trihydrates.

INTRODUCTION

The present work is part of a general scope dedicated to the study of the pyrolysis of ammonium trioxalatometallates(III), in order to get at low temperature finely dispersed simple (1,2) and/or mixed oxides (3,4). Some of these oxides, which can be original metastable phases (5,6), also exhibit magnetic (7) and electric (8) properties and are good catalysts for oxo-dehydrogenation reactions. Optimal conditions for the preparation of these solids require the precise knowledge of their thermal decomposition. Accordingly, homogeneous dispersion of the metallic elements has to be already realized in the precursor phases. The liquid-solid equilibria during crystallization, and the dehydration processes have then to be accurately established.

In the present work, the interest of using the above-mentioned techniques for the investigation of trioxalatometallates(III) is particularly emphazised. The dehydration processes of the trihydrates are then discussed in relation with their respective crystal structures.

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EXPERIMENTAL

Preparation of ammonium trioxalatometallates (III)

The preparation method used for the synthesis of ammonium trioxalatochromate(III) $(NH_4)_3[Cr(C_2O_4)_3].3H_2O$ has been derived from the one given by BAILAR and JONES in the case of the potassium complex (9), by replacing the potassium salts by the ammonium homologues. The corresponding reaction is formulated as :

$$(NH_4)_2Cr_2O_7 + 7H_2C_2O_4 + 2(NH_4)_2C_2O_4 \rightarrow 2(NH_4)_3[Cr(C_2O_4)_3].3H_2O + 6CO_2 + H_2O$$

Ammonium trioxalatoferrate(III) is obtained by dissolving ferric hydroxide in an aqueous solution of ammonium hydrogeno-oxalate. The ferric hydroxide is prepared by reaction between ammonia and ferric chloride solutions :

$$2Fe(OH)_3 + 3H_2C_2O_4 + 3(NH_4)_2C_2O_4 \rightarrow 2(NH_4)_3[Fe(C_2O_4)_3].3H_2O$$

These complexes are recrystallized twice in water. The ferrate(III) is light-sensitive, and has to be stored in a dark place, since otherwise it might be altered as a consequence of solid sate photoreduction of the Fe(III) species.

X-ray diffraction

All the phases have been characterized by chemical and X-ray powder diffraction using a SIEMENS D-500 with graphite post-monochromatized copper radiation (10). The structures of the trihydrates have been established by single-crystal investigations on an ENRAF-NONIUS CAD4 automatic diffractometer at the Henry-Longchambon Diffraction facility of our University (11,12).

TG and DTA techniques

The dehydration experiments have been performed on a SETARAM G20 thermobalance equipped with a PR 540C temperature programming device for the constant heat-rate runs. The dehydration has also been studied under constant partial water-pressure. In this later case the sample is disposed in a small reactor in the thermostat, and a water-saturated air stream coming from another thermostat is admitted on the investigated solid. For each run at a given temperature, the sample is weighed, equilibrated for 24 hours in the presence of the gaseous stream (according to the <<equilibrium points>> method [13]), and re-weighed before the next run.

For the DTA experiments a SETARAM MDTA85 analyser has been used with a 600 °C/hr heating-rate.

Crystallization phase diagrams

Besides the well-known thermal analysis, several other experimental techniques have been used. In the case of the water-ammonium trioxalatochromate(III) system, the composition of the saturated liquid phase can be obtained by visible-light spectrophotometry. The spectra of the aqueous solutions exhibit three bands at 419 , 568 and 677 nm (figure 1). The investigated system satisfies the Lambert-Beer law. The signal at 677 nm is very weak and only the two other absorption bands have been exploited (ε_{419} = 10.005 $m^2.mol^{-1}$; ε_{568} = 7.866 $m^2.mol^{-1}$).

In all cases the solubility has been determined by specific-weight (SW) and resistivity (R) measurements. At a given temperature and for a given saturated solution of known composition, the variations of SW and R are measured when small amounts of water are added to the solid-liquid system. The SW (or R) versus water-volume curve might present several discontinuities corresponding each to a different phase transition. The last discontinuity corresponds to the saturation limit. Figure 2 represents the corresponding observations for the ferrate(III) complex.

The experimental devices have already been described elsewhere (14,15,16).

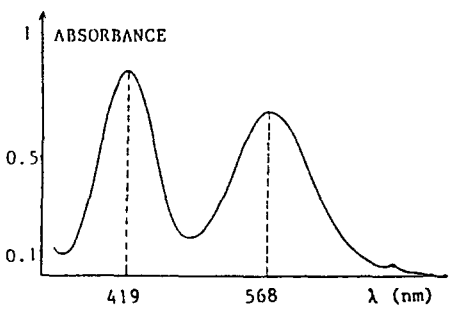

Fig.1 -Visible-light spectrophotometry of $(NH_4)_3[Cr(C_2O_4)_3].3H_2O$ aqueous solutions.

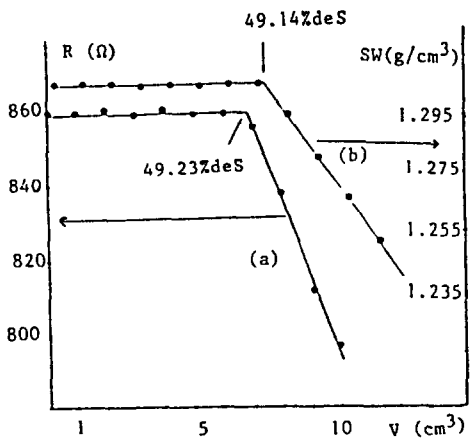

Fig.2 - a) - Variation of the conductivity
b) - Variation of the specific weight

RESULTS

Liquid-solid phase diagrams

All the results obtained by the above-mentioned techniques are very consistent and are represented on figures 3 and 4.

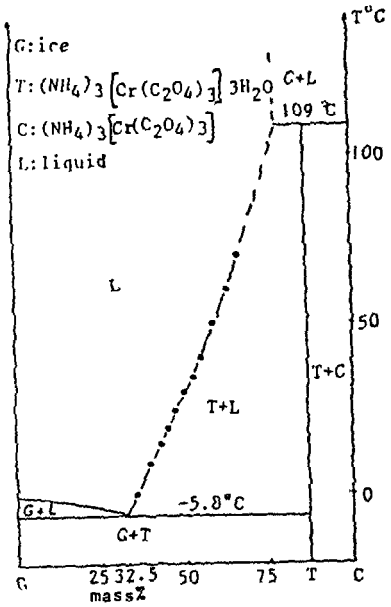

Fig.3

H_2O- $(NH_4)_3[Cr(C_2O_4)_3]$ phase diagram

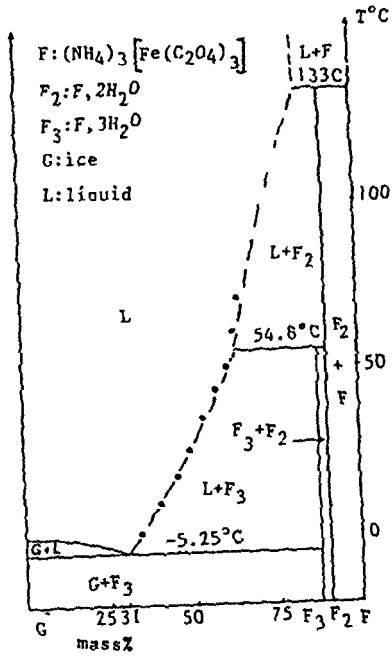

Fig.4

H_2O- $(NH_4)_3[Fe(C_2O_4)_3]$ phase diagram

The water-chromate(III) system (figure 3) reveals the existence of a non-congruently melting trihydrate with a peritectic plateau at 109°C corresponding to the trihydrate/anhydrous salt equilibrium and of a eutectic at -5.8°C for 32.5% anhydrous phase. The compositions of the saturated solutions and of the hydrate have been determined by investigating their Tamman diagrams.

In the water-ferrate(III) system (figure 4) a non-congruently melting trihydrate with a peritectic plateau at 54.8°C corresponding to the trihydrate-dihydrate equilibrium is observed. This non-congruently melting dihydrate presents a peritectic plateau at 133°C corresponding to the

dihydrate/anhydrous salt equilibrium. Except for the existence of a dihydrate in the water-ferrate(III) system, both investigated diagrams are very similar.

Dehydration of the trihydrates

The TG curves have been recorded (figure 5) with a 20°C/h heating rate. For the chromate(III) the progressive loss of the three water molecules is observed in the 25-120°C range (observed weight-loss : 12.5% ; calculated for 3 H_2O : 12.75%). In the case of the ferrate(III) the total weight-loss corresponds to 2.8 water molecules (11.9%), as already reported by BRAR et al. in (2), but the TG curve exhibits a pseudo-plateau near the 65-70°C temperature range, which might indicate at least a two-step water departure, and/or the existence of a possible plateau for the intermediate dihydrate.

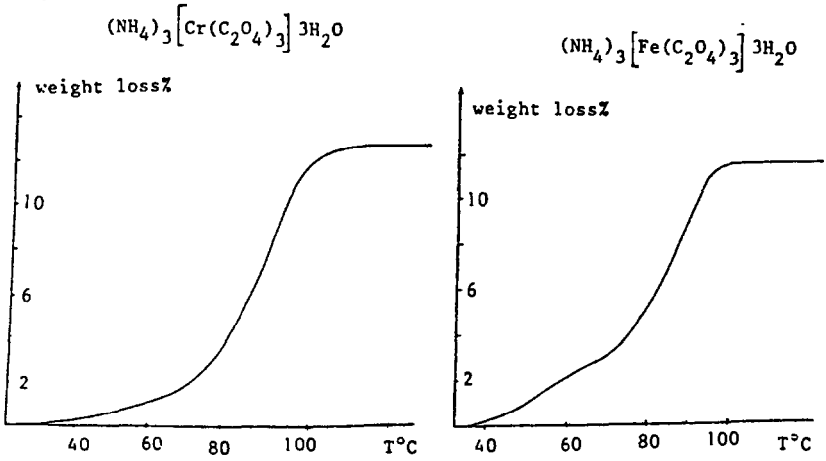

Fig.5 - TG curves for a 20°C/hr heating rate.

In order to verify this interpretation, the dehydration has been investigated under controlled partial water pressure at 1200 Pa, using the << equilibrium points>> technique during the heating and the cooling of the analyzed specimen (figure 6). For the ferrate(III) the experiment has been performed on crystals issued from a crystallizing solution just before the run. The experimental curve exhibits a plateau in the 30-40°C range, corresponding to the loss of one water molecule, and above this plateau the loss corresponds to the remaining two water molecules : accordingly, the two-step water departure and the existence of a normal trihydrate for the ferrate(III) are thus certified. The ferrate(III) is very air-sensitive, and loses part of its water content when isolated from the saturated solution. In the case

of the chromate (III), the first rapid water-loss corresponds at 50°C to nearly two water molecules, the anhydrous salt being observed at 90°C. Furthermore, in the 50-90°C range, the equilibrium is divariant.

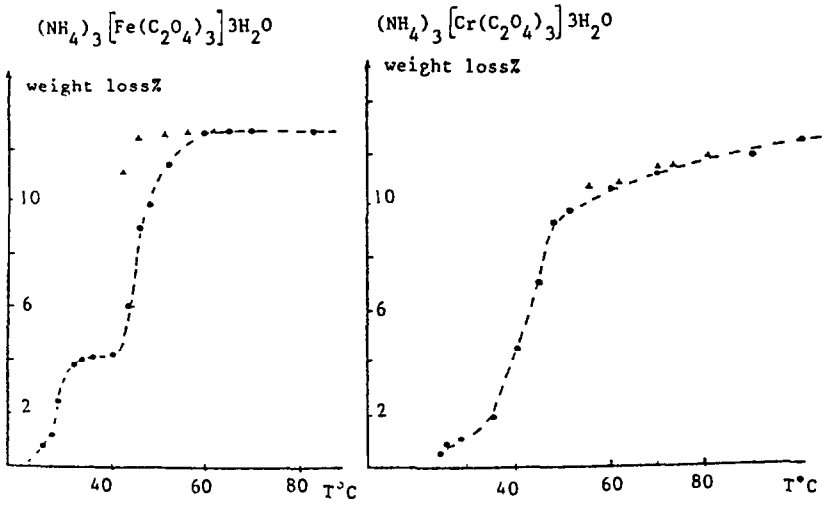

Fig.6 -TG runs under controlled water pressure at 1200 Pa - heating(O)/cooling(Δ) of the specimen.

The DTA curve for the ferrate(III) (fig. 7a) exhibits two endo-peaks. The first one is weak and is attributed to the departure of the first water molecule, which is not tightly bonded in the crystal structure. The second peak is intense and corresponds to the loss of the remaining two water molecules. In the case of the chromate(III) (fig. 7b) only one complex endo-peak presenting a shoulder at 125°C is observed.

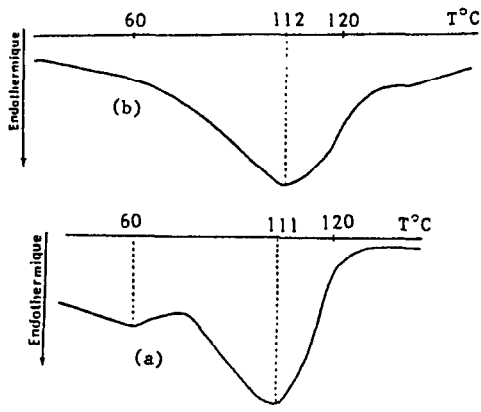

Fig.7 -DTA curves

In order to reinforce our interpretations, the water-pressure controlled TG curves have been compared on a same drawing with previously established phase-diagrams. Figure 8a corresponds to this comparison for the ferrate(III) complex, where abscissae stand for molar-fractions : it clearly appears that the dehydration processes are all within the domain corresponding to the existence of solid phases ; the characterization of the dihydrate corresponds to an abrupt temperature increase. For the chromate(III) (figure 8b), a similar situation is observed. Accordingly, our interpretations of the TG and DTA curves are consistent with the above-mentioned results.

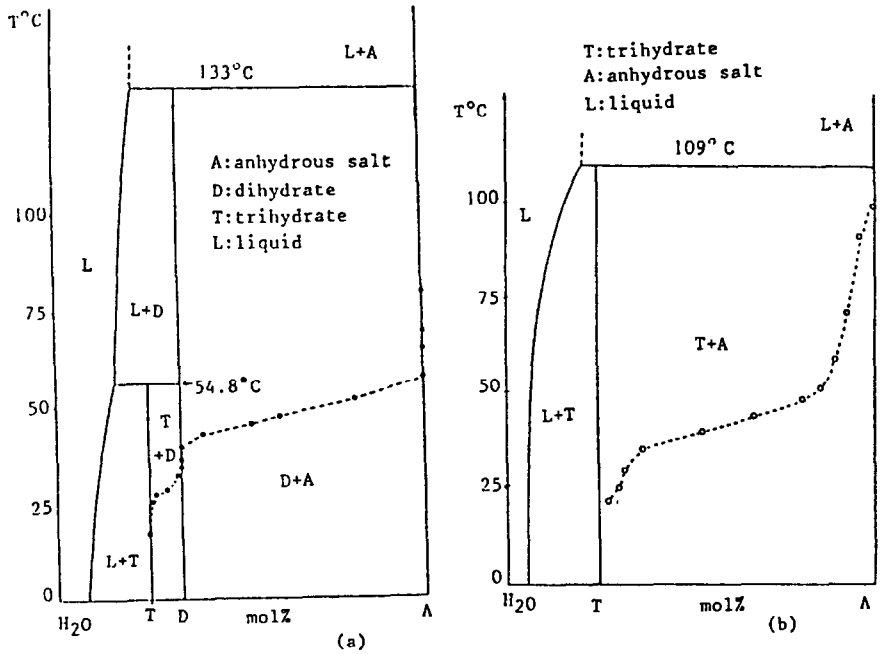

Fig.8 - Comparison of the phase diagrams with the TG curves under controlled water pressure atmosphere at 1200 Pa : for the ferrate (a) and chromate (III) (b) complexes.

Discussion of the dehydration of the trihydrates in terms of their crystal structures

Some of the crystal data concerning the investigated trihydrates are summarized here :

$(NH_4)_3[Cr(C_2O_4)_3].3H_2O$, space group $P\bar{1}$, $Z = 2$, $a = 7.857(1)$, $b = 10.667(2)$, $c = 10.694(2)$Å

$\alpha = 83.27(1)$, $\beta = 70.06(1)$, $\gamma = 70.54(1)°$, $V = 794(1)$ Å^3, $Dx = 1.773$ g.cm^{-3}

$(NH_4)_3[Fe(C_2O_4)_3].3H_2O$, space group $P2_1/c$, $Z = 4$, $a = 7.791(4)$,$b = 20.124(6)$, $c = 10.478(3)$ Å

$\beta = 106.87(3)°$, $V = 1572(2)$ $Å^3$, $Dx = 1.808 g.cm^{-3}$

Although these two complexes are not isostructural, crystal structures exhibit striking similarities (figure 9) :

- the geometry of the $[Cr(C_2O_4)_3]$ macro-anion is the same ;
- channels parallel to the [100] are observed in both cases ;
- one water molecule and one ammonium ion are respectively spread over four mutually excluding OW3A,OW3B and N3A,N3B sites ;
- in both cases one water molecule is not revealed by the difference-Fourier maps ;

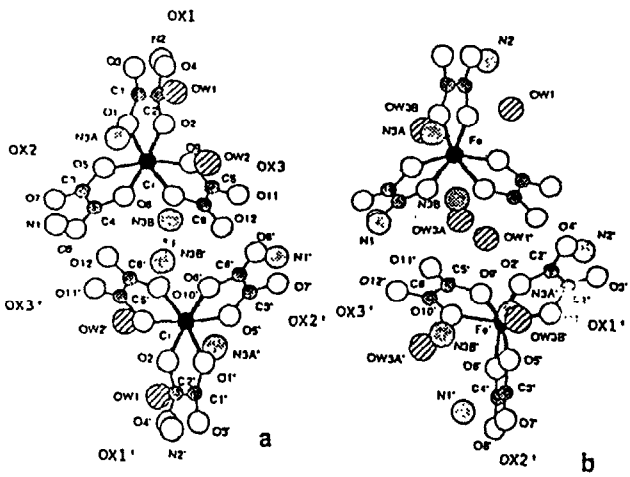

Fig.9 - Crystal structure details for the $(NH_4)_3[Cr(C_2O_4)_3].3H_2O$ (a) and $(NH_4)_3[Fe(C_2O_4)_3].3H_2O$ (b) complexes.

but there are important differences :

- in the chromate(III) the structurally characterized water molecules are both out of the channel, and it might be assumed that the third water species is spread over several partially occupied sites in the channel which is only occupied by the two symmetry-related N3B and N3B' ions.
- in the ferrate(III) OW1 and OW3A are in the channel and OW3B is very close to it. In this case we assume that the third water molecule is not in the channel but statistically disordered near the assumed possible "OW2" site (cf. chromate(III) homologue) : this structurally <<missing>> water might then correspond to the labile molecule which is already lost at low temperature, as soon as the complex is separated from its saturated solution.

Furthermore, it must be emphasized that the OW1 and OW2 water molecules in the chromate(III) complex have a relatively high Debye-Waller factor of nearly 15 $Å^2$, whereas in the ferrate(III) phase the thermal factor for the OW3A and OW3B species are nearly 5 $Å^2$, which thus correspond to tightly bonded water molecules. These remarks must also be considered in the case of the potassium (17) and rubidium (18) trioxalatochromate(III) complexes, where all the three water molecules are localized by X-ray techniques on single-crystal investigations

At this stage of our investigations we might propose some assumptions concerning the dehydration-processes of the $(NH_4)_3[Cr(C_2O_4)_3].3H_20$ and $(NH_4)_3[Fe(C_2O_4)_3].3H_20$ phases. In the chromate(III) phase the weakly bonded OW1 and OW2 molecules (cf. above) are easely evolving during the first dehydration step, and the third but undetected and tightly bonded water molecule, which is <<delocalized>> in the channel, gives rise to the divariant equilibrium observed at higher temperatures. This assumption might find some support by considering that this third water molecule is involved in possible hydrogen bonds with the protons of the N3B and N3B' ammonium ions. In $(NH_4)_3[Cr(C_2O_4)_3].3H_20$, $K_3[Cr(C_2O_4)_3].3H_20$ and $Rb_3[Cr(C_2O_4)_3].3H_20$ the OW2 water molecule is well localized but weakly-bonded (high thermal factor) ; hence, if we assume in the ferrate(III) a possible localization of a third water molecule delocalized near its potentially possible "OW2" site, its departure during the dehydration could correspond to the dihydrate-plateau observed on the TG curve of figure 6, the remaining and more tightly bonded OW1 and OW3A,OW3B molecules evolving at higher temperatures.

Further discussion of structure related properties concerning the investigated phases has now to be extended by considering also the potassium and rubidium trioxalate(III) complexes (17,18). This work is presently in progress and will be related elsewhere.

CONCLUSION

We might conlude by considering that the above mentioned results represent preliminary investigations concerning the study of theerystallization-process of hydrated ferrate(III) and chromate(III) mixed solid solutions which might then be decomposed in order to synthesize finely dispersed mixed-oxides presenting original catalytic properties.

It must also be emphasized that several problems concerning the dehydration of the investigated complexes could be resolved thanks to the knowledge of their crystal structures.

REFERENCES

(1) - D.BROADBENT, D. DOLLIMORE and J. DOLLIMORE, J. Chem. Soc., A, (1967), 451.
(2) - A.S. BRAR and B.S. RANDHAWA, J. Solid State Chem., 58, (1985), 153.
(3) - J. PÂRIS and R. PÂRIS, Bull. Soc. Chim. Fr., (1954), 1138.
(4) - A. ROUSSET, F. CHASSAGNEUX and J. PÂRIS, J. Thermal Anal., 11, (1977), 405.
(5) - A. ROUSSET, J. PÂRIS and P. MOLLARD, Ann. Chim., 7 , (1972), 119.
(6) - F. CHASSAGNEUX, G. DUPRE and A. ROUSSET, C.R.Acad.Sc., C, 293, (1981) , 437.
(7) - J. COHEN, P. MOLLARD, J. PÂRIS and A. ROUSSET, C.R.Acad.Sc.,B,268, (1969) , 1001.
(8) - B. GILLOT, F. BOUTON, F. CHASSAGNEUX and A. ROUSSET, Phys. Stat. Sol., 50, (1978) , 109.
(9) - J.C. BAILAR and E.M. JONES, Inorganic Synthesis, McGraw-Hill Book Co. Inc., N.Y., 35 (1939) , 8.
(10) - E.H. MERRACHI, B.F. MENTZEN and F. CHASSAGNEUX, Powder Data, in press.
(11) - E.H.MERRACHI, B.F.MENTZEN and F.CHASSAGNEUX, Rev. Chim. Min.,23,(1986) , 329.
(12) - E.H. MERRACHI, B.F. MENTZEN, F. CHASSAGNEUX and J. BOUIX, Rev. Chim. Min., 24, (1987) , 1.
(13) - J.C. MUTIN, G. WATELLE-MARION, Y. DUSAUSOY and J. PROTAS, Bull. Soc. Chim. Fr., 12, (1972) , 4498.
(14) - R. TENU, J.J. COUNIOUX and R. COHEN-ADAD, Bull. Soc. Chim. Fr., (1979), 84.
(15) - R. TENU and J.J. COUNIOUX, Bull. Soc. Chim. Fr., (1979) , 155.
(16) - J. BERTHET and J. SAID, L'actualité Chimique, September 1985, 57.
(17) - D. TAYLOR, Austr. J. Chem., 31, (1978) , 1455.
(18) - E.H. MERRACHI, B.F. MENTZEN and F. CHASSAGNEUX, Rev. Chim. Min, in press.