

Evolution of hydrogen on dehydroxylation of clay minerals

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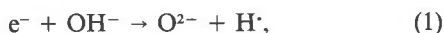
ABSTRACT

Mass spectra showed that H₂ evolved on vacuum heating of kaolinites, halloysite, and sepiolite but not on vacuum heating of the montmorillonite samples studied. Release of H₂ occurred during clay dehydroxylation, but reached its maximum at a higher temperature. It was independent of the amount of Fe²⁺ or Fe³⁺ present in the clay.

INTRODUCTION

Recent studies showed that on heating clay minerals, a variety of volatiles evolved (Keller, 1986; Heller-Kallai et al., 1988). A gas of particular interest is H₂, both because its presence can provide insights into the mechanism of clay mineral dehydroxylation and because of its reducing potential in chemical reactions; unfortunately the experimental techniques adopted in these studies were not geared to detection of this gas. Formation of H₂ on heating in air, in an inert atmosphere, or in vacuo has been observed with various hydroxyl-containing minerals, e.g., biotites and amphiboles (Hodgson et al., 1965; Kalinichenko et al., 1985; Clowe et al., 1988, and references therein) and ferrous hydroxide (Neal and Stanger, 1983, and references therein). Evolution of H₂ was attributed to (1) oxidation of Fe²⁺ by oxygen or water or (2) in either an inert atmosphere or in vacuum, autoxidation by structural hydroxyl groups. However, Yershova and Dimitriyev (1978) claimed that H₂ evolution from a series of amphiboles on vacuum heating was neither related to Fe²⁺ oxidation nor dependent on the amount of structural OH present. They concluded that trapped H₂ in the minerals was released on heating.

Few studies on H₂ evolution from clay minerals have been reported in the literature. Freund and Gentsch (1967) found that silica gel, Mg(OH)₂, Al(OH)₃, and kaolinite produced H₂ on vacuum heating, but only after most of the hydroxyl water was lost. They attributed evolution of H₂ to reactions of OH⁻ groups with "exo-electrons,"



or, in a later study on pure Mg(OH)₂ (Martens et al., 1976), to reactions between residual OH⁻ groups



and, at higher temperatures,



Both mechanisms involve lattice vacancies.

MacKenzie (1970) claimed that Mg(OH)₂, kaolinite, halloysite, and Al(OH)₃ produced H₂ only when they contained transition-metal cations or traces of C. Consequently, he attributed evolution of H₂ from hydroxyl-containing minerals in vacuum to redox reactions. Because some of his doped materials contained Fe only in the +3 state, MacKenzie postulated that reduction of Fe occurred on vacuum dehydroxylation followed by oxidation, as was previously observed for zeolites (Morice and Rees, 1968). He contended that this may be a general phenomenon in Fe-containing hydroxyl compounds. Following Freund and Gentsch (1967), he assumed that H₂ evolution occurred only after about 88% of the hydroxyl groups had been lost and preheated the samples at the dehydroxylation temperature overnight. This procedure precluded detection of any H₂ that might have formed on dehydroxylation.

Gabor et al. (1986) observed minor amounts of H₂ during dehydroxylation of kaolinite. In their mass spectra, the H₂-evolution profile does, indeed, follow that of water, but the possibility that H₂ may have formed by fragmentation of water in the spectrometer was not addressed.

The present study was undertaken to establish whether clay minerals other than kaolinite produce H₂ on vacuum heating and whether evolution of H₂ is, indeed, restricted to samples that have lost most of their hydroxyl groups.

EXPERIMENTAL DETAILS

The clay samples (Table 1) were crushed lightly and used as supplied, except for sample M(W), which was size-separated.

TABLE 1. Clay samples used

Sample	Description
K(G1)	Well-ordered kaolinite, Georgia, U.S.A. (CMS)
K(OECD-03)	Well-ordered kaolinite from Cornwall, England, used in the OECD interlaboratory study (van Olphen and Fripiat, 1979)
Hal	Halloysite, Dragon mine, Utah
Sep	Sepiolite, "Sepiolita," Tulsa, Spain
M(W)	Montmorillonite, Upton, Wyoming (CMS) <2 μm
M(CB)	Montmorillonite, Camp Berteau, Morocco

Note: CMS = clay minerals standard.

H₂ was determined with a Balzers quadrupole mass spectrometer AMG112. About 100 mg of sample, in a quartz sample holder, were evacuated overnight, heated rapidly to 100 °C, and subsequently at the rates of 25 °C/min to 620 °C, 10 °C/min from 620 to 660 °C and 5 °C/min from 660 to 700 °C. The volatiles were released into a 135-L glass tank. To avoid flooding the mass spectrometer with water, liquid N₂ was passed through spirals inside the tank, which caused most of the water to freeze. The apparatus was evacuated with a 6-in.-diameter (15.24-cm) CVC diffusion pump, with a capacity of 1400 L/min, which achieved a vacuum of 10⁻⁶ torr. During periods of intense water evolution from the sample, the vacuum was sometimes reduced to 10⁻⁵ torr or less. Because the spectrometer used had only a single channel, corresponding traces of H₂ ($m/z = 2$) and of H₂O ($m/z = 18$) were recorded in two separate runs. Great care was taken to ensure that the experimental conditions, comprising weight and grain size of the sample, evacuation procedure, the position of the thermocouple within the sample, and the heating regime, were reproducible. After each run the sample was allowed to cool in the apparatus and was reheated with the same heating program. This procedure provided traces for background corrections, which were generally small.

RESULTS AND INTERPRETATION

Figure 1 shows the $m/z = 2$ and $m/z = 18$ spectra obtained from the samples. All samples were heated beyond the dehydroxylation temperature. Cooling with liquid N₂ caused most of the water to freeze, but some water vapor persisted, as shown by the H₂O spectra. The amounts were sufficiently small not to flood the spectrometer, but a minor contribution of H₂ due to fragmentation of H₂O cannot a priori be precluded. However, the spectra obtained with sepiolite show that the strong $m/z = 18$ peak at 170 °C is not accompanied by evolution of H₂, nor was any H₂ observed when kaolinite was heated to 500 °C, when considerable amounts of H₂O were released. Under the experimental conditions adopted, therefore, no detectable contribution of H₂ is produced by fragmentation of water.

With kaolinite, halloysite, and sepiolite, evolution of H₂ overlapped dehydroxylation, though it peaked at a higher temperature (Figs. 1a, 1b, and 1c). The spectra

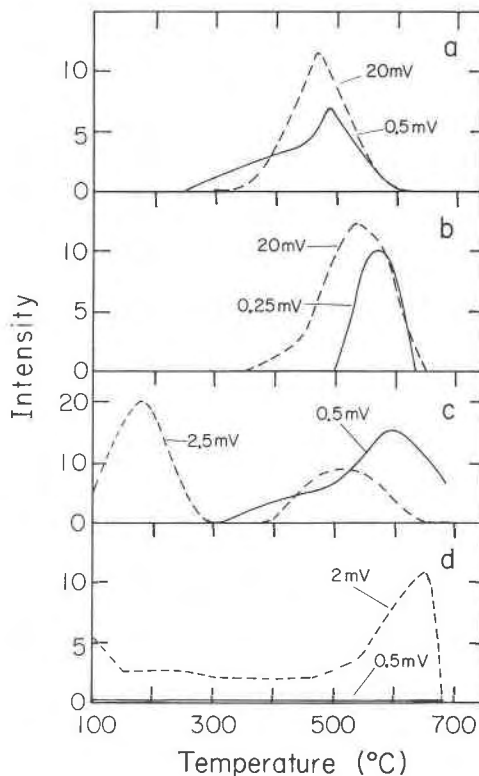


Fig. 1. Mass spectra of H₂ (solid line) and H₂O (dashed line) evolved from (a) halloysite (H); (b) kaolinite [K(G1)]; (c) sepiolite (Sep); (d) montmorillonite [M(W)]. The intensity scale is arbitrary.

obtained with sample K(OECD) resembled those of sample K(G1). Neither sample of montmorillonite produced any detectable amounts of H₂ (Fig. 1d), although they were heated beyond the dehydroxylation temperature.

The Fe²⁺ and Fe³⁺ content of the samples of montmorillonite greatly exceed those of the kaolinite and sepiolite samples studied (Table 2), yet no H₂ evolution was observed from the montmorillonites. It is apparent, therefore, that there is no correlation between the Fe content or the concentration of Fe²⁺ in the minerals and their ability to produce H₂ on vacuum heating. The presence of Fe may thus be a necessary condition for the formation of H₂, but it is certainly not a sufficient one. Moreover, Mössbauer spectra of Sep and M(W) showed that Fe²⁺ persisted on vacuum heating of both samples. The spec-

TABLE 2. Fe content of the clay samples

Sample	Fe ³⁺ (%)	Fe ²⁺ (%)
M(W)*	2.5	0.2
M(CB)*	2.3	0.2
K(G)*	0.14	0.04
K(OECD-03)*	0.37	0.04
Sep**	0.54	0.06

* Average values from van Olphen and Fripiat (1979).

** Estimated from Mössbauer spectrum.

trum of heated Sep was very blurred, even when recorded at 90 K, and could not be resolved meaningfully. The spectrum of heated M(W) was less complex; the amount of Fe²⁺ increased from 10 to 22% on vacuum heating. Evidently autoxidation did not occur with these samples, but the complexity of the spectrum of heated Sep may, perhaps, be partly due to charge transfer.

CONCLUSIONS

Small amounts of H₂ were evolved on vacuum heating of kaolinites, halloysite, and sepiolite, but not on vacuum heating of the two samples of montmorillonite examined. Under the conditions of the experiments, H₂ release overlapped dehydroxylation of the clays. Preheating clay samples at the dehydroxylation temperature before determining H₂ evolution (Freund and Gentsch, 1967; MacKenzie, 1970) should therefore be avoided.

The mechanism of H₂ evolution remains obscure. All the samples examined contained some Fe, but it was shown that there is no correlation between evolution of H₂ and the amount of Fe present, nor does autoxidation of Fe²⁺ seem to be involved. The hypothesis that H₂ is trapped in the minerals and is released on heating, as proposed for amphiboles by Yerzhova and Dimitriyev (1978), seems improbable for two reasons: (1) the temperatures at which evolution of H₂ commences are high; (2) our results, together with those for kaolinites reported in the literature, suggest that evolution of H₂ is a characteristic of clay-mineral groups (e.g., kaolinites) and not, like that of other volatiles, specific for each clay mineral.

Mass spectral analysis of the samples showed that they did not contain organic matter (Heller-Kallai et al., 1988). Another potential source of H₂ in clays is ammonia, but the amounts present in samples K(G1), K(OECD), and M(W) are similar (Keller, 1986) and cannot account for the observed differences in H₂ evolution.

The results are compatible with the concept that H₂ evolution depends on some structural properties of the clay, but whether these are defects, as proposed by Mar-

tens et al. (1976), or specific structural arrangements requires further study.

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