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FORMATION OF RALSTONITE DURING LOW-TEMPERATURE ACID DIGESTION OF SHALES[*]

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An investigation of the relation between thermal maturation and hydrocarbon generation in the western Canada sedimentary basin was partly concerned with the determination of the electron spin resonance characteristics of kerogen (insoluble organic matter) isolated from shales. A common method to concentrate kerogen from sedimentary rocks is by digestion in HCl, followed by digestion in HF, with subsequent removal of entrained pyrite by gravity separation in heavy liquids (Forsman 1963; Saxby 1970; Durand *et al.* 1972). HCl in varying concentrations (0.5*N* - 10*N*) and at a range of temperatures (20°–100°C), dissolves most carbonates, sulfides, and basic or amphoteric oxides and hydroxides; hot concentrated (48%) HF easily dissolves silicates (Saxby 1970).

HF reacts with the silicates of sedimentary rocks to produce a variety of complex fluorides. Some of these have been identified by Forsman & Hunt (1958) as potassium fluosilicate (K_2SiF_6), aluminium oxyfluoride ($Al_2OF_4 \cdot 3H_2O$) and potassium fluoaluminate (K_3AlF_6), although they found a number of X-ray diffraction reflections that could not be ascribed to definite compounds. However, they obtained indirect evidence that some of these X-ray diffraction reflections might be attributed to mixtures of complex fluorides composed of ferrous iron, ammonium ion, and hydrogen with such elements as Al, Ca, Mg, and K. They used several techniques to remove these complex fluorides, including digestion with hot HCl, hot-water extraction, and treatment with zinc and water or aqueous alkalies. Kerogen may oxidize during HF treatment with the progressive decrease in the mineral content, although this is largely prevented if the temperature remains below 60°C and the insoluble residue does not evaporate to dryness (Dancy & Giedroyc 1950; Smith 1961).

In this study shale cores were collected from a wide range of stratigraphic intervals at depths up to 3350 m. They were chipped clean and crushed in a shatterbox to pass 325 mesh. Because a hot HF digestion might increase the number of free radicals in the kerogen, the temperature was held at 40°C during all acid digestions, which also took place under nitrogen. After digestion in 2*N* HCl, the residue was centrifuged and washed with hot water until free of calcium ions. Following digestion with 48% HF, a few mls of 2*N* HCl were added to the solution, which was then diluted with a saturated boric acid solution, centrifuged, and washed with hot water. The residue was then centrifuged in a mixture of bromoform and acetone (6:1) to separate the kerogen from pyrite. X-ray diffraction showed potassium fluosilicate in all kerogen samples. This was entirely removed from the samples with copious volumes of hot water. The removal of the potassium fluosilicate revealed a second compound, other than pyrite and possibly minor K-feldspar, which is ralstonite, $Na_xMg_xAl_{2-x}(F,OH)_6 \cdot H_2O$.

Because of the intimate interrelation of the kerogen and ralstonite, and the presence of hydrogen and oxygen in kerogen, it was decided to quantitatively extract the ralstonite with 6*N* HCl at 70°C and analyze the extract for Na, Mg, and Al in lieu of the preferable analysis of separated ralstonite. Kerogens from three samples were extracted in this manner and the results are shown in Table 1. The cubic unit cells were determined with the least-squares method of Appleman *et al.* (1972). The unit cell of a fourth ralstonite was 9.920(7)Å, but because the separated kerogen contained a small amount of impurity, identified by X-ray as possibly nordstrandite, the analysis was not determined. These cell dimensions fall within the range reported by Pauly (1965) and together with the partial analyses prove that ralstonite has a variable composition. If the acid extract is neutralized with NH_4OH, the white precipitate formed is ralstonite as confirmed by X-ray dif-

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TABLE 1. PARTIAL COMPOSITION OF RALSTONITE EXTRACTED WITH 6*N* HCl from KEROGEN

Sample Number	Analysis of Extract (g moles)			Partial Formulae of Ralstonite	Unit Cell Å
	Na	Mg	Al		
K-1	0.082	0.115	0.196	$Na_{0.55}Mg_{0.76}Al_{1.31}$	9.940(6)†
RCA 65-1	0.167	0.193	0.452	$Na_{0.52}Mg_{0.61}Al_{1.42}$	9.965(6)
BH-439A*	0.112	0.136	0.311	$Na_{0.50}Mg_{0.62}Al_{1.42}$	9.976(3)

* X-ray diffraction pattern indicates possible zoned ralstonite
† Standard deviation in parenthesis

fraction analysis. Further confirmation of the presence of ralstonite in the kerogen was obtained from infrared absorption spectra. The characteristic absorption bands are similar to those reported by Povarennykh & Lebedeva (1970), who have interpreted those at 630 - 560 cm^{-1} as valence vibrations and those at 410 cm^{-1} as deformation vibrations. Bands at 1660 cm^{-1} result from water, and hydroxyl groups give additional bands between 1200 and 800 cm^{-1}.

Ralstonite is found in a variety of parageneses other than the Ivigtut cryolite deposit (Pauly 1965), including cryolite-cryolithionite pegmatites in the Ilmen Mountains, Central Kazakhstan, U.S.S.R. (Stepanov & Moleva 1962) and at the Klyuchevskaya Volcano of Kamchatka, U.S.S.R. (Naboko 1957), where it is associated with fluorite as an alteration product of basalts and andesite-basalts caused by HF in volcanic gases at 200 to 300°C. All these parageneses suggest that a relatively low-temperature, fluorine-rich, probably acid environment is conducive to the genesis of ralstonite. As far as we can determine, there are only two published reports on the synthesis of ralstonite. Emel'yanova & Zigareva (1960) reacted an aqueous solution of H_3BO_3 (~14%) and NaCl or NaF (~3%) with topaz, pyrophyllite, or kaolinite, and the oxides of the elements in tourmaline at 350-600°C and 400-3000 atm. to produce tourmaline, fayalite, chiolite, nepheline and ralstonite. Kukovskii (1962) treated palygorskite with HF, H_2SO_4, and HNO_3 for 48 hours to yield hydrous magnesium and aluminium fluorides, fluellite, and ralstonite.

Although the conditions under which Emel'yanova & Zigareva (1960) formed ralstonite do not match those suggested above, there exists the possibility that the ralstonite only formed during cooling of their bomb and not at the highest temperature and pressure quoted. With the exception of this possibility, both the previous and present studies suggest that ralstonite is a low-temperature reaction product in fluorine-rich acid environments, which is formed in the laboratory at temperatures as low as 40°C.

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