# Obituary of C.R. Masson 1922 - 1988

During the decade 1967 - 1976 noteworthy contributions to our knowledge of silicon and sulphur chemistry, to techniques of determining the biosynthesis of natural products and to elucidation of their complex structures were made at the National Research Council's laboratory in Halifax, C.R. Masson, treasurer and longtime member of the Institute, who died on 12 March 1988, played a major role in this extraordinary efflorescence. He was born on 8 September 1922 in Aberdeen and graduated from Aberdeen University in 1943. He pursued graduate studies with H.W. Melville, was awarded a Distiller's graduate scholarship and took up the investigation of molecular weight determinations of polymers by osmometry. This work initially involved modifications of the osmometer designed by Fuoss and Mead (1943), which notably included an effective thermostating device, the use of cellulose membranes biosynthesised by Acetobacter xylicum and careful attention to the manipulation of the membranes produced by this organism. The resulting instrument was used to determine the osmotic pressure developed in a number of e.g. toluene solutions of common commercially available polymers and in some cases the values of the Huggins "constant" in these systems. In the cases of samples of polyvinyl acetate in ethyl acetate it was shown that the molecular weights obtained by osmometry agreed well with those calculated from polymerisation kinetics. These results were later elaborated when the molecular weights of a series of vinyl acetate polymers of viscosities in the range 0.5-2.15 were examined by osmometry and by a light scattering method which gave values in general agreement in the range of 1-15 x 105. The Rayleigh scattering method also provided information on the polymer shapes and this was used to explain discrepancies in the molecular weights obtained by the two methods. Several years later Masson used this experience in studies of the viscosity and degradation kinetics of the naturally occurring sulphated polysaccharides carrageenin, work of considerable contemporary interest in the light of the role these materials play in ulcerative colitis (Marcus, et al. 1989).

## Free radical chemistry

In 1948 Masson came to Canada to work with E.W.R. Steacie in the National Research Council's laboratory in Ottawa. He became associated with Steacie's long standing interest in the photodecomposition of simple organic compounds in the gas phase with photoexcited ( $M(^3P_1)$ ) mercury, cadmium and zinc species. Steacie and Masson studied the photodecomposition of propane and methyl chloride and in the latter case were able to delineate the stoichiometry of the reaction and to make suggestions for the process at pressures  $\leq$  100 mm i.e.

$$Hg (6^{3}P_{1}) + CH_{3}CI = Hg (6^{1}S_{0}) + CH_{3} + CI$$

and chart the subsequent reactions of the radicals. The discerning reader of these papers will appreciate the amount of work done to produce these results and will note the observation of the sensitivity of Cl to the presence of traces of oxygen. Masson's interest in photochemical processes, initiated by lines in the mercury arc spectrum, continued when he moved into Noyes laboratory as the C. & H. Dreyfuss post-doctorate fellow at the University of Rochester, New York. There he studied the photolysis of heptan-3-one in the gas phase and confirmed earlier observations by Bamford and Norrish (1935) that the process  $(C_3H_7)_2CO \rightarrow C_2H_4 + CH_3COC_3H_7$  occurs. He also demonstrated for the first time that the radical reaction:  $(C_3H_7)_2CO = 2C_3H_7 + CO$  is important and he found evidence for 7 other products, mostly from further reactions of  $C_3H_7$  many of which he identified. This elucidation of the photochemis-

try of simple aliphatic ketones is a considerable tribute to Masson's chemical insight and experimental skill. He continued these studies after he moved to the National Research Council's laboratory in Halifax reporting on measurements of the quantum yield of CO on photolysis of di-isopropyl ketone and on further investigation of the rate of association of n-propyl radicals.

By 1965 experimental evidence was accumulating (Richardson, 1962) that confirmed the suggestions of Flood and Forland (1947) and Richardson (1955) that silicate melts were mixtures of anionic species  $\mathrm{Si_nO_{3n+1}}^{-(2n+2)}$ . Armed with this information and the theoretical work of Toop and Samis (1962), Masson proposed, on general thermodynamic grounds, a relationship for the distribution of species in silicate melts that depended on the postulated equilibrium constant of the reactions:

$$M_2SiO_4 + M_{n+1}Si_nO_{3n+1} = M_{n+2}Si_{n+1}O_{3n+4} + MO$$

which was therefore only dependent on the nature of the cationic species M. Using published data Masson showed that the calculated relationships fitted the experimental results for binary systems e.g. CaO-SiO<sub>2</sub>, CoO-SiO<sub>2</sub>, NiO-SiO<sub>2</sub> etc., well. It followed that many other thermodynamic properties of these and related systems could be predicted, including average molecular weights. Most of the assumptions in the development; some plausible, others, e.g. the absence of intramolecular reactions, less so, were similar to those used by Flory (1941) in his development of an expression to describe the distribution of oligomers derived from monomers of the type AXB<sub>2</sub> where A and B are different functional groups. The two procedures led to conclusions that differed in detail — conclusions of doubtful validity because of the simplifying assumptions made in both cases. The proposals of Masson and his colleagues led to some controversy, but much more importantly, initiated new experimental work on the chemistry of silicates and ultimately greater understanding of the properties of metallurgical slags.

Chemistry of silicates

Lentz (1964) had demonstrated that the rection,

$$M_{n+1}Si_nO_{3n+1} + (2n+2) Me_3SiCl = Si_nO_{3n+1} (SiMe_3)_{2n+2} + (n+1)MCl_2$$

proceeded in aqueous solution, in heterogeneous systems and that the products were volatile. Masson undertook a detailed investigation of this reaction, work typical of the elegant experimental techniques that characterized all he did. Thus hemimorphite  $(Zn_4(OH)_2Si_2O_2 \cdot H_2O)$  under the conditions used by Lentz gave the trimethylsilyl derivatives of  $SiO_4^{-4}$ ,  $Si_2O_7^{-6}$ ,  $Si_3O_{10}^{-8}$  and  $Si_4O_{12}^{-8}$  in the proportions 29:27:15:29 and Masson demonstrated that the time and temperature of the reaction and the proportion of hydrochloric acid in the reaction mixture initiated reactions in the silicate before trimethylsilylation. Based on these observations a reaction protocol was developed that produced partially silylated entities as intermediates, the reaction being completed in the presence of an Amberlyst ion exchange resin. This resulted in hemimorphite being converted into its hexatrimethylsilyl derivative with less than 4% trimethylsilylated byproducts. Structural information about the trimethylsilylated silicates was obtained by mass spectroscopy. The trimethylsilyl ethers were collected as they emerged from the chromatography column in an ingenious trap, in capillaries that could be directly inserted into the electron impact source of the mass spectrometer. It was shown that the ions reactions:

$$Si-O \xrightarrow{\text{Si}-\text{Me}} \longrightarrow Si-O=Si\text{Me}_2 + \text{Me}$$

$$CH_2 \xrightarrow{\text{H}} \longrightarrow Si-O + CH_2=Si\text{Me}_2 + H$$

were of high probability; the ions of highest molecular weight undergoing at least the first of these fragmentations. Studies with fluorosilicates also showed that the process:

where X = F or  $OSiMe_3$ , for example occurred with high probability (There are a number of errors in J. Chem. Soc. (Dalton Trans.) 1979, 457; e.g. Figs 4 & 5 are transposed). This work provided information on the purity of the samples under study, their molecular weights and the presence or absence of fluorinated species. This mass spectroscopy greatly extended the use of the technique in inorganic chemistry, though mass spectrometer sources used for such purposes had a short life.

The analogous reaction:  $M_{n+1}Si_nO_{3n+1} + (2n+2)Me_3GeCl$  was also studied and its products, the derivatives  $Si_nO_{3n+1}$  ( $GeMe_3$ )<sub>2n+2</sub> characterized in the same manner. However, the yields obtained were not so good e.g.  $SiO_4(GeMe_3)_4$  was obtained in 80% yield from calcium orthosilicate, and further exploitation of this interesting variant was not pursued.

The technique of trimethylsilylation was exploited in several directions. In mineralology notable contributions to our knowledge of the structures of olivine, forsterite, tephroite, fayalite, andradite, laumontite and dioptase were made. Spectacularly, it was shown that olivine was present in lunar samples collected (lunar latitudes and longitudes) at 1°N 25°E (Apollo 11); 0°S 22°W (Apollo 12) and at 5° 30′S 17° 30′W (Apollo 14), one of the first demonstrations of the extraterrestrial applicability of the law of constant proportions. The technique was also used in some interesting aspects of soil mineralology, e.g. an analysis of imogolite, an aluminium silicate with an unusual tubular structure. This work showed that useful information could be obtained on intractable non-crystalline solids and semi-solids, e.g. cement paste, and was therefore ideally suited for investigations of the compositions of metallurgical slags and glasses.

### Metallurgy

In 1954, insufficient research and development work was being done in Canada on the chemistry of metallurgical processes despite the economic importance of the industry. In response to recommendations by a National Research Council Associate Committee and by the chairman of the British Iron and Steel Research Association, a small group of physical chemists was created to work in this field and Masson was asked to lead the group. For the purpose of this review of Masson's work, it is convenient to divide the metallurgical studies that ensued into two parts; that dealing with gas-liquid metal interactions and that dealing with the thermodynamics of metallurgical slags. Of course both lines of work were closely intertwined, especially in the experimental techniques that Masson and his collaborators devised and developed to study processes occurring in the temperature range 1000-2000°C.

# Studies of gas-metal systems

Rates of reactions are of great monetary importance in the commercial operation of metallurgical processes, and in steelmaking the most important rate is that of decarburization of iron-carbon melts. In his early metallurgical work Masson studied this rate, as well as the rate of desulphurization of such liquid alloys, and showed that they were controlled by diffusion of reactants or products in the gas phase. A novel

electrochemical cell was used to follow the kinetics of the dissolution of oxygen into liquid silver, where the rate determining step was shown to be diffusion in the liquid metal. Such kinetic research was taken up by a colleague and continued for many years as an important part of the work of Masson's group.

In his systematic study of gas-metal interactions, Masson first examined the thermodynamic activity of the metal oxide component of MO-SiO<sub>2</sub> melts. One technique for measuring such activities required determining the small (0.001-0.02%) amounts of oxygen that would dissolve in a metal phase in equilibrium with the slag. These techniques involved considerable experimental difficulties and were subject to errors, and Masson carried out a great deal of work to improve the existing methods e.g. vacuum fusion (Sloman, 1959) and isotope dilution (Kirshenbaum and Grosse, 1952) were carefully compared. Analogous investigations into the determination of oxygen in titanium at 1850°C by isotope dilution were reported.

The thermodynamic reference for the activity of FeO was the solubility of oxygen in iron when the latter was in equilibrium with pure FeO. The latter was difficult to obtain — crucibles tend to dissolve in FeO at 1600°C! Masson developed a levitation method which got rid of the necessity to use a crucible, and then pushed the reference solubility up to the hitherto unapproachable temperature of 1960°C.

## Constitution of Metallurgical Slags

In the 1950's questions were being directed towards the constitution of metallurgical slags in order to rationalize their behaviour as e.g. desulphurizing and dephosphorizing agents towards liquid iron alloys. What was a molten calcium silicate slag like at the molecular level — what were the bonds, what were the aggregations? Masson began to answer some of these questions by applying physical chemical techniques at high temperatures. For example he used the method of depression of freezing point, with molten alkali and alkaline earth fluorides as solvents, to measure the molecular weights of silicate slags. The experiments were difficult, and required ingenious solutions. Masson prepared the purest calcium fluoride then known by the bold expedient of bubbling anhydrous hydrogen fluoride through molten calcium fluoride at 1300°C, the equipment being made of graphite in the hot zone and teflon in the cold.

Another high temperature adaptation of a standard physical chemical method was the use of EMF cells. In the late 1950's Masson used magnesium oxide as an oxygen electrode to measure the oxygen potential of open-hearth slags. This was pioneering work which anticipated by several years the German development of doped zirconium oxide as a thermodynamically acceptable oxygen electrode material. For this work Masson developed an ingenious double-compartment concentration cell slip cast and sintered out of magnesia. This marked the beginning of a line of research in ceramics at the Atlantic Research Laboratory.

While polymer-ionic theory of slag constitution was being developed, Masson and his collaborators carried out a wide range of experiments to determine the polymerization constants for various systems. These methods depended on finding the thermodynamic activity of the metal oxide component of silicate and silico-phosphate melts. In some experiments slag and metal phases were equilibrated, with the oxygen content of the metal giving a measure of the activity of metal oxide. These experiments were carried out in specially selected and fabricated ceramic crucibles, as well as by levitation.

In other types of experiment an EMF cell was used to measure activities. Both oxygen (doped zirconia) and fluoride (CaF<sub>2</sub>) electrolytes were utilized. A great deal of work was done on the lead systems PbO/SiO<sub>2</sub>/P<sub>2</sub>O<sub>5</sub> and PbO/PbF<sub>2</sub>/SiO<sub>2</sub>, partly stimulated by the lead-silver development in New Brunswick. This work included activity measurements of plumbous oxide in PbO/SiO<sub>2</sub>/P<sub>2</sub>O<sub>5</sub> solution with up to 12.5

mole  $\% P_2O_5$  in the temperature range 1050-1350°C. It was shown that substitution of silica by phosphorus pentoxide reduces the activity of plumbous oxide and leads to increasing the negative partial heats of mixing of the oxide. The solubility and transport of oxygen through and from these melts and evidence that the reaction:

$$2Pb^{+2} + O_2 = 2Pb^{+4} + 20^{-2}$$

occurred in these slags were also studied in detail. Finally this work was extended to the system PbO/PbF $_2$ /SiO $_2$  and details of the equilibria between the various silicate and fluorosilicate species were delineated to the point that the value of 0.4  $\pm$  0.025) of the equilibrium constant for the reaction series:

$$F^- + Si_nO_{3n+1-m} F_m^{-(2n+2-m)} = Si_nO_{cn-m} F_{m+1}^{-(2n+1-m)} + O^{-2}$$

was estimated for basic melts. These studies utilized electrochemical methods where the crucible slip-cast from calcium fluoride was used as the solid electrolyte (F¯ being solely responsible for conduction) between the PbO/PbF<sub>2</sub>/SiO<sub>2</sub> and PbO/PbF<sub>2</sub> half cells. In many ways this work paves the way for the preparation of pure compounds of the type  $Si_nO_{3n-m}F_{m+1}X_{2n+1-m}$  i.e. a completely novel series of inorganic compounds.

The foregoing sketch of 40 years of scientific effort by Charles Masson does scant justice to his achievement. Belatedly this was recognized by the Alcan award of the Canadian Institute of Mining and Metallurgy and by his election to the Royal Society of Canada. Browsing through his list of publications one is aware of their international flavour. Some of this work was done in laboratories outside the National Research Council and conversely many post-doctorate students of Masson can now be found doing productive work in the United States, Europe and the Far East. Those of us who were his colleagues over a more extended period are aware of our loss and we extend our sympathies to his wife and family.

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