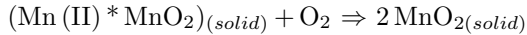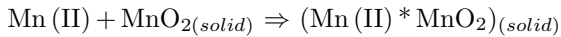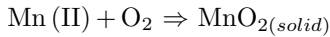# Indirect Concentration Measurement of ^{53}Mn in Ocean Water using a Chemical Separation of Mn^{+2} and Mn^{+4} from Ferromanganese Crusts or Sediments

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Measurements of long-lived radioisotopes like ^{53}Mn in terrestrial formations have fundamental applications for a number of science areas. ^{53}Mn is produced in extraterrestrial matter like cosmic dust by nuclear reactions of cosmic rays. Measurements of its concentration can be used for the determination of the flux of extraterrestrial matter onto earth, the intensity of cosmic radiation and the dating of terrestrial formations [1,2]. In addition it would be interesting to reconstruct in which chemical form ^{53}Mn and therefore cosmic dust is incorporated into the terrestrial formation, i. e. if the dust particles are directly incorporated or first dissolved. We propose a method how AMS measurements of ^{53}Mn in hydrogenetic ferromanganese crust and sediment can answer this question.

We used a chemical leaching method [3] to separate two known oxidation states of manganese, Mn^{+2} and Mn^{+4} from a hydrogenetic ferromanganese crust and a sediment in order to determine the chemical form of the extraterrestrial ^{53}Mn in the ocean; bound in dust particles or dissolved in the water. The important property of manganese are the two valence states, reduced Mn^{+2} and oxidized Mn^{+4}. The reduced Mn^{+2} state is enriched in the oxygen minimum zone of the oceanic water column. In oxidation conditions manganese is taken up from the water as Mn^{+4} into the solid mineral phase. On the other hand Mn^{+4} compounds are instable under reducing conditions and manganese is reduced to the Mn^{+2} form and accumulated again in the oceanic water:

$$Mn\,(II) + O_2 \Rightarrow MnO_{2(solid)}$$

$$Mn\,(II) + MnO_{2(solid)} \Rightarrow (Mn\,(II)\,{}^*MnO_2)_{(solid)}$$

$$(Mn\,(II)\,{}^*MnO_2)_{(solid)} + O_2 \Rightarrow 2\,MnO_{2(solid)}$$

Thus, we have in the solid form only manganese in the (IV+) state and in the oceanic water dissolved manganese in the (II+) state. Therefore manganese forms crusts and sediments only in the Mn^{+4} form. But Mn^{+2} can be incorporated in the pore water of a crust and sediment too, because the crust is very porous on well the upper layer of the sediment.Consequently, if we separate these two phases of manganese, Mn^{+4} from solid crust's or sediment's phase and Mn^{+2} from the pore water we can measure the concentrations of ^{53}Mn in both phases. These give information about the chemical form, particle like or dissolved, of the extraterrestrial matter in the oceanic water. Manganese in extraterrestrial dust is in the (II+) state. On the other hand we can estimate indirectly the concentration of ^{53}Mn in the oceanic water.

The chemical leaching method for the separation of Mn^{+2} and Mn^{+4} is based on the property of oxidized Mn^{+4} in 2% H$_2$SO$_4$ acid to stay undissolved and of reduced Mn^{+2} to be leached into dilution. Therefore, the surface of one crust (DS111) and the upper interval of a sediment (26KL) from the Pacific were leached in 2% H$_2$SO$_4$ for about 12 hours at room temperature. After the first step only Mn^{+4} should stay in the solid phase and in the solution only Mn^{+2}. The next step was the evaporation and the dissolution of the solid phase in 32% hydrochloric acids (HCl) and 65% nitric acid (HNO$_3$). The last step was extraction of the manganese from both fractions with an ion exchange chromatography and measurements of ^{53}Mn with AMS. The result is demonstrated in Tab. 1. The fraction of Mn^{+2} from the crust DS111 by the chemical extraction was lost.

sample	fraction	^{53}Mn/^{55}Mn
26KL (sediment)	Mn^{+2}	$1.1^{+1.0}_{-0.5} \times 10^{-13}$
	Mn^{+4}	$5.4^{+1.6}_{-0.6} \times 10^{-14}$
	complete	$1.3^{+0.4}_{-0.4} \times 10^{-13}$
DS111 (crust)	Mn^{+2}	-
	Mn^{+4}	$2.7^{+0.6}_{-0.3} \times 10^{-13}$
	complete	$2.3^{+0.4}_{-0.4} \times 10^{-13}$

Table 1: The ^{53}Mn/^{55}Mn ratio in the two leaching phases and the complete samples of the two selected formations.

These first measurements show the possibility to separate Mn^{+2} and Mn^{+4} from the crust and the sediment. But for the interpretation of the first results we need better statistics in the ^{53}Mn measurement and an improvement of our chemistry with the help of Cu or Zn as catalyst [4] for a better and definite separation of the Mn^{+2} fraction from the ferromanganese crust and sediment.

References

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