Development of a new facility for dating old groundwaters and ice cores based on ⁸¹Kr measurement

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Mainly produced on Earth by nuclear reactions induced by cosmic rays in the atmosphere, the radionuclide ⁸¹Kr $(t_{1/2}=229, 000yr)$ is considered as the best tracer for absolute dating of old groundwater or ice core [1, 2]. Reliable residence times have been already determined by using AMS [3] and ATTA [4] techniques. Due to the extremely low concentration of ⁸¹Kr in groundwater (<1200 atoms/L), dating requires large water samples (>2000L). CNAB has developed a set of instruments and lines designed for measuring 81Kr and 85Kr in 20L groundwater sample. Isotopic analysis of Kr is performed by using resonance ionization spectroscopy - time of flight mass spectrometry coupled with an atom buncher device [5, 6] operating at 20K in order to enhanced ionization efficiency and sensitivity, allowing precise measurement of a few thousands atoms of Kr [7]. In the case of Kr gas extracted from groundwater sample, a preliminary step performing a strong isotopic enrichment for ⁸¹Kr, ⁸⁵Kr is necessary in order to decrease the abundance ratio Kr/81Kr by a factor of 106. For this purpose, a mass spectrometer based on a modified PT2 instrument from VG has been built, which includes a specially designed FEBIAD-type source capable to produced high Kr beam current (>50nA) with high transmission efficiency and a mass resolution of 240. Krypton-81 and ⁸⁵Kr ions are collected by implantation on separate sapphires coated with a thin Al layer. Calibrations with air samples are currently in progress to optimize enrichment efficiency before processing groundwater samples.

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Pressure induced redox reactions in FeCO₃

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Iron carbonate, FeCO₃, decomposed at 35 GPa after heating at lower than 1500K; the decomposition pressure could be lower as suggested by earlier shock compression studies [1, 2], since the inefficiency of laser heating before the breakdown might also have prevented an earlier reaction in the compression cycle. Iron phases were studied using synchrotron radiation with powder, multigrain and single crystal techniques according to the variable size of the crystallites obtained in the experiment. Fe₃O₄, in the high pressure orthorhombic structure, was detected as a breakdown product and we argue that the iron oxydation occurred through partial reduction of carbon. Upon decompression to 10 GPa and heating to 1800 K the redox reaction could be partially reverted.

Deep Earth major phases exhert a strong control on the iron speciation. Even though further studies are necessary to accurately define Fe-C-O redox exchanges in mantle assemblies, redox exhanges of this type are in agreement with the general considerations consensus on deep carbon speciation, but have not yet been clearly identified. The shifting of redox equilibria with pressure in the Fe-C-O system has remarkable implications. In particular it might define a boundary for the stability of carbonates and CO_2 , which can explain greater carbon subduction compared to hydrogen [3] and the development of C-O fluid phases from the uplifting of reduced carbon bearing rocks.

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