

GEOLOGICAL APPLICATIONS OF ^{81}Kr DATING

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INTRODUCTION

Krypton possesses two extremely low-abundance radioactive isotopes. These are cosmogenic ^{81}Kr ($^{81}\text{Kr}/\text{Kr} = 10^{-12}$, $t_{1/2} = 229000$ yr), and fissionogenic ^{85}Kr ($^{85}\text{Kr}/\text{Kr} = 10^{-11}$, $t_{1/2} = 10.8$ yr). Due to its atmophile nature, Kr predominantly resides in the atmosphere and becomes isotopically well-mixed within a few years. These noble gas radionuclides serve as chronometers when atmospheric Kr is entrapped (or partitioned) and subsequently isolated in a reservoir such as glacial ice, groundwater or seawater; they have been recognized as the best available tracers of hydrological ventilation age. Atom trap trace analysis (ATTA)¹⁻³ is currently the only established method of determining the isotopic abundance of ^{81}Kr , first developed at Argonne National Laboratory. In this contribution, we discuss a new application of these tracers in the study of volcanic gases. Noble gases, being chemically inert, are the best tracers of physical processes such as mixing and phase separation, e.g., the degassing of solid Earth to form the atmosphere. The discovery of a potentially pristine mantle noble gas reservoir^{4,5} implied that our knowledge of how the Earth and its surface evolved can be improved by studying the volatile components of Earth's interior emitted via volcanoes.

Being atmophile elements, noble gases predominantly reside in the atmosphere. Their concentrations in the mantle are low, and analysis of noble gases in mantle-derived materials is prone to atmospheric contamination. In order to better constrain the mantle end-member in volcanic gas samples, it is essential to resolve the source of atmospheric contamination. The studies of past three decades have shown that it is practically impossible to unambiguously distinguish the different types of atmospheric components in mantle-derived gas samples by looking at the stable isotopic compositions of noble gases. Use of radioactive isotopes of Kr is expected to determine the nature of the atmospheric contamination because the apparent age of the contaminating atmosphere is a good indicator of the type of contamination.

Atmosphere contaminated during sampling has "zero" age at which all noble gas radionuclides have modern isotopic abundances. Relatively "young" (~1,000-10,000 yr) atmosphere is expected for the contamination during gas transport in the crust involving dissolved air in groundwater, where ^{85}Kr will be negligible and ^{81}Kr abundance will be near that of modern air. Assimilation by magma of crustal components (including hydrosphere) is a more complicated process to identify, but understanding the regional geology and hydrology would help in deciphering the isotopic signature of crustal assimilation. By avoiding the locations related to aged (> 20,000 yr) groundwater, which applies to most volcanic provinces, the abundance of ^{81}Kr

would be an indicator of atmospheric contamination from crust. At the timescale of subduction (~ 10^6 - 10^7 yr), all air-derived noble gas radionuclides would have decayed to negligible abundances; thus, a ^{81}Kr -free noble gas sample would be the best indicator of subduction-recycled atmospheric component. Krypton-85 isotopic abundance will be useful in determining the fraction of very young atmospheric contamination (e.g., direct incorporation of atmospheric air) vs. the total superficial atmospheric contamination determined by ^{81}Kr , through which we learn the dominant atmospheric contamination process.

EXPERIMENTAL DEVELOPMENTS & RESULTS

It has been conventional practice for the analysis of noble gas radionuclides to sample bulk gas in the field and separate out Kr in the laboratory³. In case of groundwater studies, the concentrations of Kr and Ar in the dissolved air-like bulk gases are 1-4 ppm and 1-2%, respectively. To assure that the required quantities of Kr (~50 μLSTP) are obtained, > 50 liter STP of bulk gas is usually sampled. The situation is significantly different for volcanic and thermal gases as they consist predominantly of CO_2 , so 100-200 times more total gas sample is necessary for the analysis. Because it is not practical to transport such large quantities of gas, we developed a simple on-site system for condensation of H_2O and removal of CO_2 . On the gas emanations, a large (~20 inches in diameter) Teflon funnel was placed. A Teflon tubing of 1/2 in. diameter was connected to the funnel and carried the gas through a cooling coil and a large Pyrex condenser bulb submerged in a cold water bath. The gas was then pumped by a vacuum compressor through a large U-shaped steel tube filled with pellets of "soda-lime" CO_2 absorbent. Using this system, we successfully sampled Kr in sufficient quantities for the analysis of noble gas radionuclides from three geothermal features at Yellowstone National Park.

A system for Kr purification from large-volume water and gas samples was developed at the University of Illinois at Chicago. This system consists of cryogenic distillation, gas chromatographic separation and Ti-gettering, allowing relatively rapid (4-6 hours) separation of pure Kr with high yield (>90%) from a large range of bulk gas quantities (5-125 liter STP). It includes an in-line gas composition monitoring capability using a quadrupole mass spectrometer. Kr in the amounts of 19, 22 and 76 μLSTP were successfully separated from the above-mentioned Yellowstone samples to be analyzed by an improved ATTA instrument.

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