^{40}Ar-^{39}Ar dating of sedimentary rocks and constraints on the evolution of the ^{40}Ar/^{36}Ar ratio of the Earth's atmosphere

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Degassing models of the Earth require a rather fast early evolution of the major features of the atmosphere followed by slower degassing (1). This development can potentially be revealed by studying the change of the atmospheric Ar isotopic composition with time to its present ratio ^{40}Ar/^{36}Ar=295.5. Since the primordial ^{40}Ar/^{36}Ar-ratio is not higher than $(2.9 \pm 1.7)10^{-4}$ (2), all atmospheric ^{36}Ar is primordial and ^{40}Ar stems from ^{40}K decay inside the solid Earth. The atmospheric ^{40}Ar/^{36}Ar ratio must then have increased to 295.5 between the formation the Earth, 4.5 Ga ago and the presence by degassing of the Earth's crust and the partially degassed upper mantle. The evolution of atmospheric ^{40}Ar/^{36}Ar thus is intimately coupled to the thermal history of the solid Earth. Ancient atmosphere can be trapped in sediments and hence be studied. The analysis of Ar trapped in sedimentary rocks from the Precambrian atmosphere, however, is rather difficult: secondary losses of *in-situ* radiogenic Ar have to be taken into account as well as possible excess argon components mobilized or introduced during such secondary events.

We conducted a thorough, stepwise heating ^{40}Ar-^{39}Ar study of a variety of sedimentary rocks, 21 samples in total, from the Witwatersrand, the Transvaal, and the Fig Tree groups at the Kapvaal Craton, South Africa as well as two Shungites from Karelia (3).

All the Witwatersrand and Transvaal samples were thermally reset 2Ga ago at the emplacement of the Bushveld complex, or were overprinted even later, while these events did not completely reset the K-Ar clock of any of the Fig Tree samples. From the Witwatersrand unit we measured samples of a drill core at the Loraine Mine, Oranje Freistaat Goldfield, Witwatersrand, South Africa (4). As expected from the overprint there is no correlation of age and depth. One of the quartzites features a well defined age plateau at 2.14 ± 0.01 Ga, in complete agreement with a potassium-rich (10 000 ppm) shale sample and a further sample from underlying units. The thucholithe samples have consistent ages, however, with distinct irregularities in the age spectra (Fig. 1). A K-poor quartz sample (32 ± 3 ppm K) has excess ages ranging from 6 to 12 Ga.

A K-rich shale from the Transvaal sequence gives a well constrained age of 2.18 ± 0.02 Ga with minor gas losses in the initial temperature fractions, while the adjacent K-poor chert shows ages exceeding 2.5 Ga. Kerogen separate ages from the shale range from 3 to 11 Ga. The amounts of excess argon present in

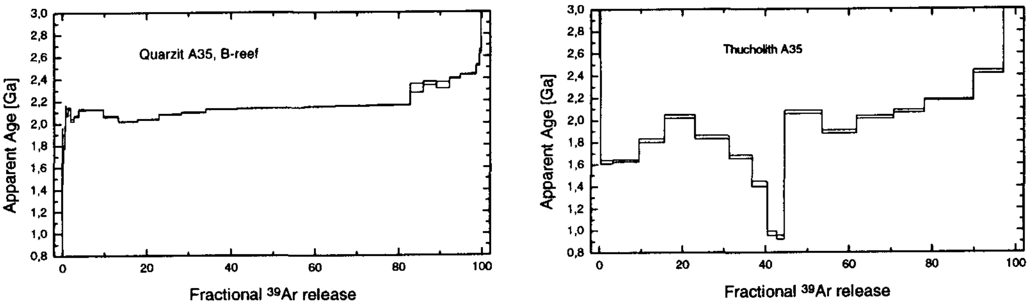

FIG. 1. Age spectra of a quartzite and an adjacent thucholithe from the Loraine Gold Mine drill core.

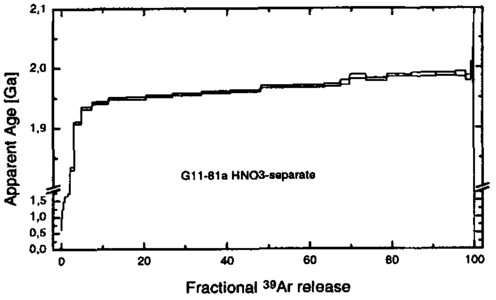

FIG. 2. Age spectrum of the acid residue.

the kerogen and the chert can be explained by incorporation of radiogenic argon lost by the shale.

Two lithologies from a banded iron formation unexpectedly are only 0.6 ± 0.07 and 1.1 Ga old as inferred from the minimum ages of their saddle shaped spectra. This hints at influences of panafrican activity on the K-Ar system.

We further analysed an acid-residue consisting of quartz and most probably illite which was obtained from a carbonaceous rock and provides a very well defined plateau age of 1.940 ± 0.004 Ga (Fig. 2).

From the Fig Tree group we analysed a shale and a grit from a drill core that have ages of ~2.7 Ga, while the kerogen from the shale again has a 'plateau-like' age spectrum in excess ages of 10 Ga. Here again ^{40}Ar redistribution can account for the minor excess age of grit and the major excess of kerogen. A light chert of another drill core yielded an age of 2.46 ± 0.2 Ga, while a dark chert showed a saddle shaped age spectrum with a maximum age close to 2.6 Ga.

Shungite samples from Karelia (3) with a stratigraphic age of 2 Ga are known to contain large amounts of trapped Ar. As expected, the age spectra were not useful in obtaining geochronological information, but some constraints on the evolution of the ^{40}Ar/^{36}Ar ratio in the atmosphere are possible. While type-5 shungite had a moderately high ^{36}Ar content of 11.310^{-8} ccm STP, our sample of type-1 shungite contained almost 10^{-5} ccm STP ^{36}Ar. Radiogenic and excess argon together contributed only a few percent to its total amount. ^{40}Ar/^{36}Ar ratios of both shungites in the initial degassing fractions are significantly below the present atmosphere. It still has to be investigated if they are caused by fractionation or if indeed they represent ancient atmosphere.

The only South African sample where ancient atmosphere may be present is a magnetite separate from banded iron formation sample ECB8 from the Witwatersrand unit. Taking all temperature fractions, the isochron gives a low initial ^{40}Ar/^{36}Ar ratio and an age of 2.045 ± 0.011 Ga. However, the non-ideal age spectrum reveals slight loss of radiogenic Ar in the initial extraction fractions and subsequently some indications of ^{39}Ar-recoil. It has to be modelled if one or both effects can result in the initial ^{40}Ar/^{36}Ar ratio below 295.5.

References

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