Cosmic-Ray-Produced Neon at the Surface of the Earth

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Abstract. Cosmic-ray-produced nuclides in terrestrial rocks can provide information on surface exposure time, erosion rates, and glacial cover. In the case of $^{21}\text{Ne}$, the cosmic-ray-produced component represents one of several components, and a component resolution based on three-isotope correlations is essential. We developed analytical techniques which permit accurate corrections for all interfering ions. We show that ratios doubly charged/singly charged ions are not constant. The spallation ratio $(^{22}\text{Ne}/^{21}\text{Ne})_c$ of $1.243 \pm 0.022$ from Si is confirmed in other quartz separates from Trans-Antarctic sandstones. This ratio is expected to be essentially constant for terrestrial quartz samples and will be useful in component resolutions. Cosmic-ray-produced Ne is released at rather low temperatures and the stepwise release permits partial separation from trapped and nucleogenic components. Trapped Ne isotopic abundances in quartz separates from these Antarctic sandstones do not generally agree with those of atmospheric Ne, and the evolved signatures reveal incorporation of nucleogenic Ne as well as fractionated trapped components.

1. Introduction

During the past few years new methods have been developed for studies of cosmic-ray-produced nuclides in terrestrial rocks, which are expected to provide important geomorphological and glaciological information such as surface exposure ages, erosion rates, and extent of glacial cover (CRAIG and POREDA, 1986; GRAF et al., 1991; KURZ, 1986; MARTI and CRAIG, 1987; NIEDERMANN et al., 1993; NISHIZUMI et al., 1986; PHILLIPS et al., 1986). The rates of nuclide production as well as erosion models were reviewed by CERLING and CRAIG (1994) and LAL (1991). The production rates of these nuclides are two to three orders of magnitude lower than in extraterrestrial materials because of the cosmic ray attenuation in the Earth’s atmosphere. Furthermore, they vary depending on irradiation conditions, such as shielding and irradiation geometry, and of course altitude and latitude.

The stable nuclides $^3\text{He}$ and $^{21}\text{Ne}$ are not only produced by cosmic ray reactions, but can be formed in situ by $(\alpha,n)$-reactions or by neutrons, as these rocks contain U, Th and other $\alpha$-emitters, or can be incorporated as trapped or nucleogenic com-

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ponents during formation or metamorphism of the rocks. Cosmic-ray-produced $^{21}\text{Ne}$ ($^{21}\text{Ne}_c$) was first identified in the summit lavas of the Haleakala volcano (Marti and Craig, 1987). $^{21}\text{Ne}_c$ not only permits studies of exposure histories beyond the limit of a few million years imposed by the $^{10}\text{Be}$ and $^{26}\text{Al}$ half-lives, but is expected to reveal complexities due to varying production rates, such as expected from a variable ice cover. A component identification based on three isotope correlations is required (Niedermann et al., 1993) and additional parameters (stepwise release at increasing temperatures, grain size separates) are also useful (Niedermann et al., 1994). Products from nuclear reactions may contribute significantly, because these represent integral inventories produced over time scales sometimes significantly longer than the time of exposure to cosmic rays.

Figure 1 shows schematically the Ne isotopic systematics expected from in situ produced components due to ($\alpha$,n) and cosmic ray reactions, based on the assumption that only one trapped (e.g., atmospheric) Ne component is present initially. The ratio of cosmic ray produced ($^{22}\text{Ne}/^{21}\text{Ne}$)$_c$ is from Niedermann et al. (1993).

Experimental determinations of production rates have been carried out for the radionuclides $^{10}\text{Be}$ and $^{26}\text{Al}$ in quartz from glacially polished granitic rocks from the Sierra Nevada (Nishiiizumi et al., 1989) and for $^3\text{He}$ (Kurz et al., 1990; Poreda and

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![Diagram](attachment:image.png)

Fig. 1. This figure shows the Ne three-isotope systematics and the directions of shifts expected from the addition of nucleogenic and cosmic-ray-produced spallation components. The $^{20}\text{Ne}$-normalization is used for experimental reasons (high precision) and because trapped $^{20}\text{Ne}$ is least affected by the spallation and ($\alpha$,n) reactions. The spallation ratio ($^{22}\text{Ne}/^{21}\text{Ne}$)$_c = 1.243$ is from Niedermann et al. (1993) and is confirmed in this work.
CERLING, 1992) in dated lava flows. Production rates of cosmogenic $^{21}$Ne are currently not well known, but may be estimated from $^3$He/$^{21}$Ne spallation ratios and from production rate ratios (MICHEL et al., 1991; LAL, 1991; POREDA and CERLING, 1992). NIEDERMANN et al. (1994) have shown that theoretical production ratios $P_{21}/P_{26}$ (of $^{21}$Ne$_c$ and $^{26}$Al) for Si targets are underestimating this ratio. However, observed ratios are in rather good agreement with calculated cosmic ray production ratios in extraterrestrial materials (MICHEL et al., 1991). This indicates that the ratio $P_{21}/P_{26}$ is relatively insensitive to the energy spectrum of secondary cosmic rays at the Earth’s surface.

The isolation of the spallation Ne component requires a correction for the trapped component. Trapped Ne refers to the isotopic composition of Ne incorporated at the time of closure of the system for Ne. At this time any Ne components which previously had formed, may be included as integral part of “trapped” Ne. NIEDERMANN et al. (1994) reported isotopic signatures observed in quartz samples from the Sierra Nevada and these authors considered the possibility that more than one trapped component may be present. The identification of multiple trapped components proved to be rather difficult, since nucleogenic components due to ($\alpha$,n) reactions on O and F made significant contributions to the total Ne inventory.

Isotopic shifts due to these nucleogenic components were observed to be much smaller in Allan Hills quartz (NIEDERMANN et al., 1993). We will further investigate the signatures of cosmogenic Ne$_c$, as well as trapped Ne, which are obtained from isotopic shifts in documented rocks from the Allan Hills and Wright Valley region of Antarctica. We address some experimental issues which affect the isotopic signatures of trapped Ne. The isotopic abundances of Ne in these and other Antarctic samples will be discussed in detail elsewhere.

2. Sample Selection and Gas Extraction

All Ne measurements were carried out in aliquots of quartz separates previously analyzed for $^{10}$Be and $^{26}$Al. The sampling areas and the geology of these samples were discussed by NISHIIZUMI et al. (1991). The Allan Hills ALH 85-2 quartz sandstone was from a boulder in the Mawson Formation, sampled 4 m above the present ice shield at an altitude of 1955 m, Allan Hills ALH 85-8 was obtained from the Beacon Sandstone outcrop at an altitude of 1615 m, and Wright Valley Beacon Supergroup sandstone sample BW 85-109 at an altitude of 1850 m.

All rock samples were ground to <700 $\mu$m and quartz was separated by selective chemical dissolution (KOHL and NISHIIZUMI, 1992) This process removes 5–15 $\mu$m from individual quartz crystals and, therefore, most recoils from surrounding minerals. Quartz separates of 0.6–0.8 g were used in this work.

For the detection of small numbers of cosmic ray produced Ne atoms, an extraction technique and a mass spectrometer with very low analytical blanks are required. For this purpose an all metal extraction furnace with a Ta foil resistance heater was used. Temperature calibration was performed by using the melting points of Zn, Al, and Au; simultaneously the temperature was controlled pyrometrically.

Ne blanks have atmospheric composition and correspond to $<2 \times 10^7$ atoms $^{20}$Ne
(<7 × 10^4 atoms 21Ne) at room temperature and about twice as much at 1000°C.

Gases are successively purified in two steps: first on two Ti sponges at decreasing temperatures (700–400°C) and then on an additional SAES getter. After Ar, Kr, and Xe are frozen to a stainless steel frit at boiling nitrogen temperature, Ne is collected on a cryogenic charcoal finger at 35 K and analyzed after He. Our modified VG 5400 mass spectrometer is equipped with two additional SAES getters. The mass spectrometer sensitivity and mass discrimination are determined by analyzing air pipettes containing 7.5 × 10^{10} atoms of 20Ne.

3. Charge State Distributions

NIEDERMANN et al. (1993) noted that at low partial pressures of Ar the ratio of doubly and singly charged 40Ar ions is not constant in our ion source, as is generally assumed. Precise interference corrections on 20Ne require calibrations of the 40Ar^+/40Ar^+ ratio. A similar problem also exists for the interference correction on 22Ne due to a non-constant ratio CO₂^+/CO₂^+, which was traced to depend predominantly on the residual H₂ background in the mass spectrometer. NIEDERMANN

![Graph](image)

**Fig. 2.** Figure 2 shows that the ratio of the charge states Ar⁺ and Ar⁰⁺ is not constant, and that it depends on the composition of the mass spectrometer background. The figure reveals a good second order fit for a background parameter x = [H₂⁺] + α[CO₂⁺] (for our instrument α = 5.71 × 10⁻³; H₂⁺ is measured in volts on the Faraday detector and CO₂⁺ on the Daly detector).
et al. (1993) also noted that although the charge state ratios were linearly correlated with the partial pressure of H₂ in the mass spectrometer, these ratios changed in a systematic way over a one-year period. We have studied these dependences in more detail and found that long-term changes were mainly reflecting a drop of the CO₂ partial pressure. A parameter which combines the partial pressures of H₂ and of CO₂ offers much better control of charge state changes. Figures 2 and 3 show recent calibrations of the charge state ratio of Ar and CO₂ for a background parameter \( x = [H₂^+] + \alpha[CO₂^+] \), both ions measured as peak heights (in V, using the Faraday detector for H₂⁺ and the Daly detector for CO₂⁺). The ratios of Ar (Fig. 2) and of CO₂ (Fig. 3) charge states are fitted by second order polynomials, and in both cases the fits are very good, with an uncertainty of only ±1%. Thus, monitoring of the H₂ and CO₂ backgrounds in our VG 5400 permits accurate interference corrections for both ⁴⁰Ar⁺⁺ and CO₂⁺⁺ and yields high precision Ne isotope ratios even for very small samples. The potential interference by the hydride ion ²⁰NeH⁺ and ²¹Ne⁺ was discussed by NIEDERMANN et al. (1993). It is small as long as the H₂ background is kept low. At the m/e = 20 position there are also the interfering ions H¹⁹F⁺ and H₂¹⁸O⁺, which can be resolved (at resolution ~600) by accurate determinations of the mass position for ²⁰Ne measurements (NIEDERMANN et al., 1993). A very reproducible

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\frac{CO₂⁺⁺}{CO₂⁺⁺} = 49.25 + 453.7 \times - 1084.4 \times x^2 
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Fig. 3. This figure is similar to Fig. 2, but shows the dependence of the ratio of the charge states for CO₂⁺⁺ and CO₂⁺⁺ on the background in our mass spectrometer. For background parameter \( x \), see Fig. 2.
mass position (0.003 amu) for $^{20}$Ne measurements can be obtained by centering the $\text{H}_2^{16}\text{O}^+$ and $\text{CO}_2^+$ peaks in every measurement cycle.

We further calibrated the Ne and Ar sensitivities of the instrument at low partial pressures and found that changes in the charge states can affect concentration measurements which are based on peak heights of Ne$^+$ and Ar$^+$, respectively. This non-linearity is relatively small (<3%) for Ne, since Ne$^{++}$/Ne$^+$ ratios are much smaller than Ar$^{++}$/Ar$^+$ ratios. Better linearities are obtained by using the sums (Ne$^+$ + Ne$^{++}$) or (Ar$^+$ + Ar$^{++}$) respectively, for peak height calibrations.

4. Cosmic-Ray-Produced Ne

The slope of the mixing line in Fig. 1 labeled “cosmic-ray spallation” was obtained as 1.120 ± 0.021 from a detailed study of separated quartz samples from Antarctic sandstone boulder ALH 85-4 (NIEDERMANN et al., 1993). These authors used a production ratio (in Si) ($^{21}\text{Ne}/^{20}\text{Ne}$)$_c = 0.8 \pm 0.1$ and obtained a ratio ($^{22}\text{Ne}/^{21}\text{Ne}$)$_c = 1.243 \pm 0.022$. This ratio can be expected to be almost constant for terrestrial quartz samples, because the energy spectrum of cosmic rays becomes essentially invariant at atmospheric depths >200 g cm$^{-2}$ and negative muon captures are not a significant contribution to the Ne production from Si (LAL, 1991). The dashed line shown in Fig. 4 has the same slope and represents the mixing line shown in Fig. 1, of atmospheric Ne and cosmic-ray-produced Ne$^c$. The low temperature (350°C) Ne fractions account for most of the $^{21}\text{Ne}_c$ concentrations which range from 34 to 95 Mat g$^{-1}$ quartz (1 Mat = 10$^6$ atoms). In two of the three samples plotted in Fig. 4, the data plot on or close to the dashed line and are consistent with mixtures of atmospheric Ne and a spallation component with this signature, identified in ALH 85-4. We note that the shifts due to spallation Ne are well reproduced in the present samples, and that the isotopic signature of ($^{22}\text{Ne}/^{21}\text{Ne}$)$_c$ apparently is rather constant. Figure 4 also reveals shifts away from the mixing line. Offsets are apparent in the 350°C fraction of ALH 85-8 and in all medium temperature (620°C) fractions. These offsets may indicate the presence of nucleogenic $^{21}\text{Ne}_n$. However, the high temperature (1600°C) data of the ALH samples require another explanation, as discussed later.

Measured $^{21}\text{Ne}_c$ concentrations can only be translated into rock exposure times at the surface of the Earth if the production rates are known. NIEDERMANN et al. (1994) determined the production ratio $P_{21}/P_{26}$ in two quartz samples of Sierra Nevada granites, which were brought to the surface by glacial scouring during the Tioga period of the last ice age. They obtained a ratio $P_{21}/P_{26} = 0.65 \pm 0.11$. Sample ALH 85-2 reveals a shorter exposure time than other Antarctic rocks (NISHIIZUMI et al., 1991) which is less dependent on the erosional history. GRAF et al. (1991) discussed the $^{21}\text{Ne}/^{26}\text{Al}$ evolution lines for Antarctic rocks and varying erosion rates. We measured a concentration of $^{21}\text{Ne}_c = 38 \pm 4$ Mat (10$^6$ atoms) g$^{-1}$ quartz and together with the $^{26}\text{Al}$ concentration of 52 ± 3 Mat g$^{-1}$ quartz (NISHIIZUMI et al. 1991), calculate production ratios, which are consistent with $P_{21}/P_{26} = 0.65$ for a range of possible erosion rates. This datum appears to support the $P_{21}/P_{26}$ ratio obtained by NIEDERMANN et al. (1994).
5. Trapped Ne Components in Quartz

The ratios $^{21}\text{Ne}/^{20}\text{Ne}$ in all 1600°C fractions shown in Fig. 4 are larger than in atmospheric Ne and the ratios $^{22}\text{Ne}/^{20}\text{Ne}$ in the 1600°C fractions of the ALH samples are smaller than in atmospheric Ne. Contributions to the $^{21}\text{Ne}$ budget by $^{21}\text{Ne}_n$ components due to $^{18}\text{O}(\alpha,n)$ reaction should be expected in relatively old rock, and $^{22}\text{Ne}_n$ additions due to $^{19}\text{F}(\alpha,n)$ are also possible, but not the observed deficits in Fig. 4. Significant nucleogenic ($^{21}\text{Ne}_n$ and $^{22}\text{Ne}_n$) components were observed in quartz separates of Sierra Nevada granites which were exposed to cosmic rays only recently ($\sim 10^3$ a), but had a long ($\geq 10^8$ a) prehistory of $\alpha$-particle reactions from U and Th decays (NIEDERMANN et al., 1994). These authors also observed $^{22}\text{Ne}/^{20}\text{Ne}$ ratios smaller than the atmospheric value in some temperature fractions and concluded that a distinct trapped Ne component is required to explain the records. A similar situation is indicated in the present study. During the complex geologic sequences of mountain building and uplifts in the Trans-Antarctic mountains, pre-existing distinct components of nucleogenic and of fractionated atmospheric Ne may have been incorporated into forming rocks as "evolved trapped" Ne components. This does not necessarily require that atmospheric Ne at that time was different, as
fractionation processes by diffusion and incomplete transfers during recycling can be invoked. The Ne isotopic records in Fig. 4 can be explained in principle by a three-component mixture of cosmic-ray-produced Ne and two trapped components, one of atmospheric composition and one with a sub-atmospheric $^{22}\text{Ne}/^{20}\text{Ne}$ ratio. It is possible that the Ne records actually involve more than three components, but such information would require detailed studies on grain size and density separates, of the type performed on Sierra Nevada granites (NIEDERMANN et al., 1994).

6. Conclusions

We have shown that the spallation Ne signature can be identified in quartz separates of Antarctic sandstones. It is consistent with the value $(^{22}\text{Ne}/^{21}\text{Ne})_c = 1.243$ reported by NIEDERMANN et al. (1993). Precise interference corrections for doubly charged ions require calibrations of the charge state distributions of interfering ions in the mass spectrometer. We show that the assumption of an atmospheric signature for trapped Ne is in general incorrect, as a fraction of trapped Ne in our quartz samples is “evolved”, i.e. at times of system openings additional in situ produced and fractionated Ne components may have been incorporated and added to atmospheric Ne.

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