
SHORT COMMUNICATIONS

ANCIENT SUN WAS HIGHLY ACTIVE

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THE pyroxene mineral separate from gas-rich meteorite, Kapoeta, has been studied using a noble gas mass-spectrometer to decipher the solar cosmic ray (SCR) proton fluxes and energy spectra, emanating from the ancient sun, during the early solar system. This sample has been etched to remove the solar wind (SW) and the resulting mixtures of solar flare (SF), solar and galactic cosmic ray (SCR and GCR) neon have been resolved into individual components by a new method developed in this study. The results indicate that (a) the ratio of solar to galactic cosmic ray spallation neon in etched Kapoeta pyroxenes is about 14 at 0.4 g cm^{-2} shielding depth and (b) the SCR proton fluxes from the ancient sun are about 3 to 4 orders of magnitude higher than those obtained from the contemporary sun.

Results based on different investigations suggest that the ancient sun may be very active during the formation of our solar system¹⁻³. An investigation of a gas-rich meteorite, Kapoeta, is ideally suited for the study of solar activity during the early solar system. The dark portions of these meteorites contain the records of the ancient sun about 4 to 4.5 b.y. ago^{2,4} while the records in lunar soil samples are considered to represent the recent past of our sun⁵⁻⁸. Neon isotopic studies in both gas-rich meteorites and lunar samples provide clues to solar flare effects as neon consists of different components with characteristic isotopic compositions such as implanted SW-Ne and SF-Ne components and SCR and GCR spallation neon components⁵⁻⁷.

A method has been developed to resolve the SF, SCR and GCR neon mixtures (after SW removal by chemical etching of the silicate grains) into individual components in the case of etched pyroxene mineral separates from the dark portions of Kapoeta, in order to decipher the SCR proton fluxes of the ancient sun.

A pyroxene mineral fraction, from the Kapoeta meteorite free from feldspars, has been separated using heavy liquid separation method. This mineral separate (90-200 μ) was chemically etched to remove the surficial SW. The etched sample was separately wrapped in

Al-foil and step-wise heated and analyzed in a UHV-glass mass-spectrometer using standard procedures^{5,6,9}.

The neon data, obtained for etched Kapoeta pyroxenes, are plotted in figure 1. The data points, representing the first temperature fractions, *i.e.* 600°C, plot much below the SF-Ne end point clearly indicating the complete removal of SW-Ne by etching.

The SCR spallation effects in the etched mineral residue were quantitatively estimated using the following method:

The total (*t*) neon, obtained from the stepwise heating analysis of the etched mineral residue (after removing SW) is given by $(21) t = (21) \text{ SF} + (21) \text{ GCR} + (21) \text{ SCR}$ and similarly for the other neon isotopes. GCR exposure age of the dark (D) portion of the gas-rich meteorite to be same as the light (L) portion *i.e.* GCR age (D) = GCR age (L) was considered. From the observed total Ne, the GCR-Ne equivalent, as obtained from the light portion analysis (or cosmogenic ²⁶Al or ⁵³Mn exposure age equivalent) is subtracted. The resulting Ne content in the sample thus consists of two components *i.e.* SF and SCR. The corrected 20/22 and 21/22 ratios are plotted in the inset of figure 1. The resulting point R in the inset of figure 1, is joined to the SF-Ne point and extrapolated downwards to intersect the SCR-field (pyroxene) at a point S representing the average shielding depth at which the irradiated grains of the gas-rich meteorite had undergone SF-irradiation, before compaction, *n* the regolith of the meteorite parent body. The amounts of SF and SCR are determined by the position of R on the line joining SF-R-S. The composition of SF-Ne used here¹⁴ is 11.6 ± 0.2 which is similar to that obtained from our earlier studies on mineral separator from lunar fines^{6,7}.

For Kapoeta pyroxenes, we used a GCR exposure age of 2.5 million years¹⁰ and subtracted the equivalent GCR spallation from the total neon observed in the etched mineral sample. The corrected neon ratios (20/22 = 8.25 and 21/22 = 0.266) are plotted in the inset of figure 1. By the above method, we find that, for Kapoeta pyroxenes, the average shielding depth for SCR irradiation is $\sim 0.4 \text{ g cm}^{-2}$ and the ratio of SF-²¹Ne to SCR-²¹Ne is 64.4; 35.6. Using these values, we deduce that the SCR-²¹Ne in Kapoeta to be $0.323 \times 10^{-8} \text{ cc/g}$ and the ratio of SCR-²¹Ne to GCR-²¹Ne is 0.404. When we apply the correction due to the fraction of irradiated

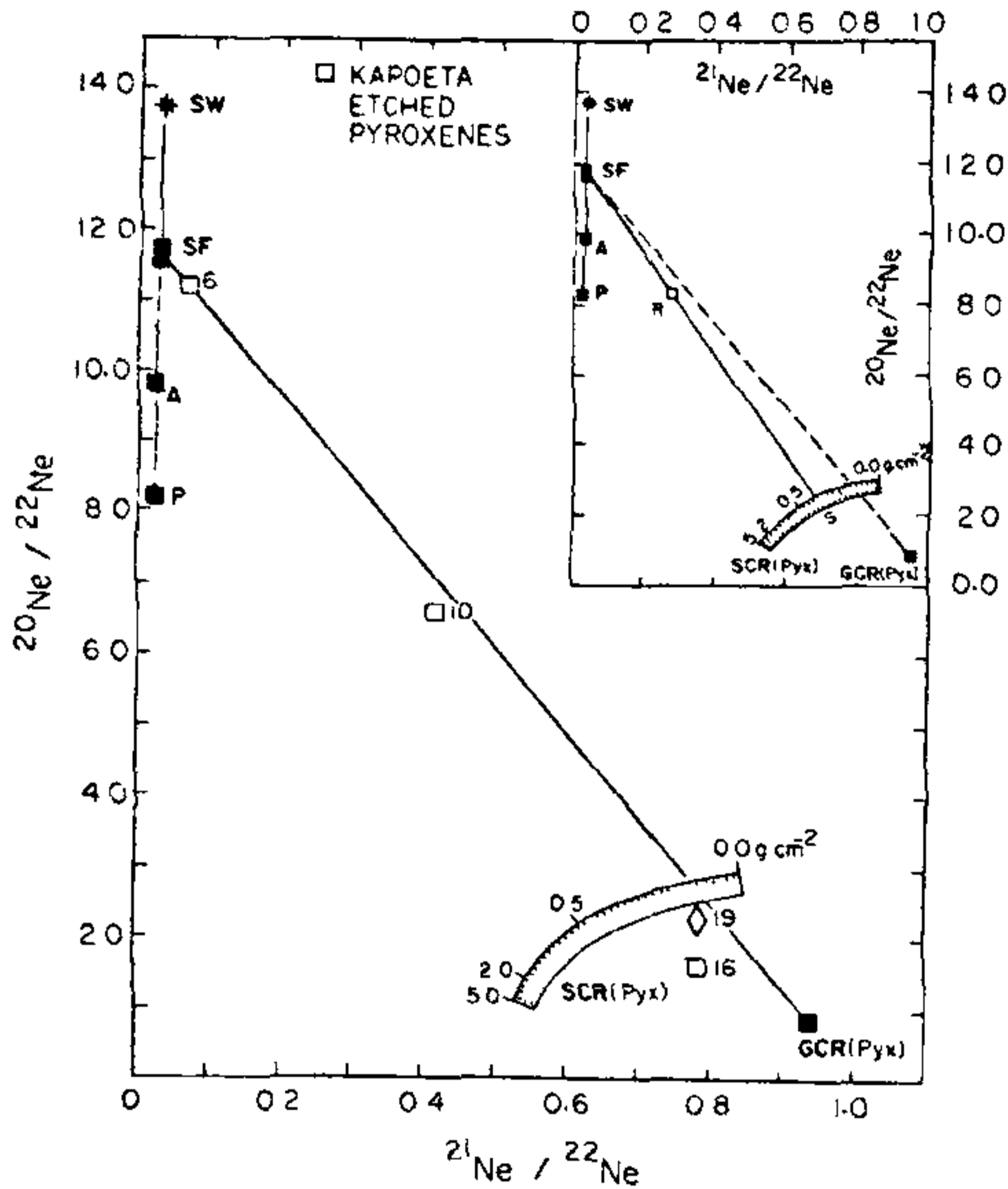


Figure 1. Neon diagram in which the data points representing the three component system (SF, SCR and GCR) for etched Kapoeta pyroxenes, are plotted. SW, SF, A and P refer to solar wind, solar flare, atmosphere and planetary neon compositions. GCR (Pyx) end-point refers to pyroxene neon values ($^{20}/^{22} = 0.84$; $^{21}/^{22} = 0.94$) determined by Lugmair *et al*¹³. SCR (Pyx) field shown by dotted band is calculated for pyroxenes using data of Hohenberg *et al*¹¹. The diamond point refers to the irradiated pyroxene grains from Kapoeta of Caffee *et al*². The numerals near the data points refer to the temperature in hundreds of degree centigrade. In the inset of figure 1, the point representing two component system (SF and SCR), after GCR corrections, for Kapoeta are plotted and it is denoted by "R" in the text. The point of intersection of the line joining SF and "R" with the SCR (Pyx) field is denoted as "S" which determines the average shielding depth of the irradiated grains.

grains ($N_H/N = 0.03$) in Kapoeta, the ratio of SCR- ^{21}Ne to GCR- ^{21}Ne works-out to be 13.5 at $\sim 0.4 \text{ g.cm}^{-2}$ shielding depth.

From the data of Hohenberg *et al*¹¹ based on the average contemporary SCR proton flux at 1 A.U., SCR- ^{21}Ne production rate versus depth profiles for pyroxenes in these gas-rich meteorites were obtained. Using these curves, the average ^{21}Ne -SCR production rates

were estimated for the shielding depth, obtained above, in the case of Kapoeta *i.e.* $0.292 \times 10^{-8} \text{ cc STP g}^{-1} \text{ m.y.}^{-1}$. Using these data, SCR- ^{21}Ne exposure age of Kapoeta pyroxenes were estimated to be 36.9 m.y. This value holds good for 1 A.U. fluxes and at 3 A.U. where the gas-rich meteorites were presumably formed, the SCR- ^{21}Ne age turns out to be an order of magnitude larger *i.e.* 369 m.y. This duration of SCR irradiation for grains in Kapoeta is very high. It is clearly inconsistent with the present knowledge of asteroidal and planetary regolith models. The average near surface residence times for silicate grains in lunar regolith is about a few million years or less and in the regolith of meteorite parent bodies, these residence times are expected to be $\sim 10^5$ years¹². It appears that the very high SCR exposure age, found for Kapoeta is due to the fact that low SCR- ^{21}Ne production rates, or in other words, low SCR-proton fluxes based on the contemporary values at 1 A.U. are used in our calculations. If the proton fluxes (taking the energy spectrum to be the same) at the time and place of SCR irradiation on the parent body regolith of Kapoeta meteorite are about three to four orders of magnitude larger than what they are today at 1 A.U., then the pre-compaction ages of SCR-irradiation for the gas-rich meteorites (dark portions) work out to be a million years or less. This suggests that the solar flare activity during the evolutionary period of the early sun may be about 3 to 4 orders of magnitude higher compared to the SF activity in the recent past.

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hydrogen bonds made by water II. Adjacent chains are bonded by weaker hydrogen bonds by water I. The factor group analysis predicts 333 (excluding 3 acoustic modes) vibrational modes at $k = 0$.

$$\Gamma_{333} = 42 A_g + 42 B_{1g} + 42 B_{2g} + 42 B_{3g} \\ + 42 A_u^{(o)} + 41 B_{1u} + 41 B_{2u} + 41 B_{3u}$$

The g modes are Raman active and u modes except A_u are infrared active. The highest possible symmetry of HPO_4^{2-} ion (considered as HOPO_3^{2-}) is C_{3v} , corresponding to free rotation of the hydroxyl group about its P-O bond⁵. Of the 12 internal modes of HPO_4^{2-} ion, $9(3A_1 + 3E)$ are associated with PO_4 group and 3 with OH group. These modes are both IR and Raman active.

In the crystal, the HPO_4^{2-} ions occupy sites of lower symmetry than its free ion symmetry (C_{3v}). This leads to anisotropic crystal field which removes the degeneracies of the normal modes. The non-degenerate PO_3 symmetrical stretching mode, correlated to A_1 species of the PO_4^{3-} ion with T_d symmetry splits into two components both in IR and Raman (table 1). The splitting of this nondegenerate mode is due to the resonance interaction between vibrating ions of the unit cell. Two types of HPO_4^{2-} ions producing these two lines are not possible, since no doubling of lines corresponding to other stretching modes is observed. The P-O(H) stretching mode (A_1) and PO_3 asymmetric stretching mode (E) are derived from the triple degenerate P-O asymmetric stretching mode (F_2) of PO_4 group with T_d symmetry. The bands observed due to these modes are strong both in IR and Raman.

In order to assign the deformation vibration of HPO_4^{2-} ion, it has been assumed that the bending modes of HPO_4^{2-} ion consist of $\delta_{as} \text{PO}_3(E)$, $\delta_s \text{PO}_3(A_1)$ and $\delta \text{P(OH)}(E)$ vibrations. Bands due to these modes have appeared in the $390\text{--}600 \text{ cm}^{-1}$ region. The relationship between ν_{OH} and $r(\text{O-H})$ suggests an OH stretching frequency in the $2700\text{--}3000 \text{ cm}^{-1}$ region⁶. The band at 2910 (IR and Raman) has been assigned to (P) O-H stretching mode. The bands at 2440 and 2330 cm^{-1} (IR) are taken as combinations.

The two doublets in the OH stretching region of water indicates two crystallographically distinct types of water molecules in the crystal. The bands corresponding to each water molecule have been assigned on the basis of their hydrogen bond strength. The bands in the $450\text{--}700 \text{ cm}^{-1}$ region have been tentatively assigned to librational modes of water⁷. The OPO bending modes have also been observed in this region.

VIBRATIONAL SPECTRUM OF $\text{Na}_2\text{HPO}_4 \cdot 2\text{H}_2\text{O}$

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COMPOUNDS in the series $\text{Na}_2\text{HPO}_4 \cdot n\text{H}_2\text{O}$ ($n = 0, 2, 7, 12$) are of considerable interest and have been the subject of extensive experimental investigations¹⁻⁴. X-ray structural studies of $\text{Na}_2\text{HPO}_4 \cdot 2\text{H}_2\text{O}$ have indicated the presence of two distinct types of water molecules and the nature of hydrogen and coordination bonds in the crystal². Chapman and Thirlwell⁴ from their IR analysis showed two distinct HPO_4^{2-} ions in $\text{Na}_2\text{HPO}_4 \cdot 2\text{H}_2\text{O}$ contrary to the x-ray results. A vibrational study has been attempted to resolve the ambiguities in the structure and to understand the dynamics of the crystal.

The IR spectrum of the sample prepared as KBr pellet has been recorded on a Perkin-Elmer 283 spectrophotometer. A SPEX Ramalog 1401 equipped with a Spectra Physics model 165 Ar^+ laser (5145 \AA line with $100\text{--}200 \text{ MW}$) has been used to record the spectrum.

$\text{Na}_2\text{HPO}_4 \cdot 2\text{H}_2\text{O}$ crystallizes in an orthorhombic system with space group Pbca (D_{2h}^{15}) and has eight molecules in the unit cell². Sodium atoms and HPO_4^{2-} ions are in general positions. The two water molecules occupy crystallographically non-equivalent C_1 sites. HPO_4^{2-} groups are linked into an infinite chain by the