review article

γ-Ray line astronomy

R. Ramaty*

McDonnell Center for the Space Sciences, Washington University, St Louis, Missouri 63130

R. E. Lingenfelter

Astronomy Department, University of California, Los Angeles, California 90024

γ-Ray astronomy is a valuable source of information on solar activity, supernovae and nucleosynthesis. Cosmic γ-ray lines were first observed from solar flares and more recently from the galactic centre and a transient event. The latter may give an important insight into nuclear reactions taking place near neutron stars and black holes and a measure of the gravitational redshifts of such objects.

γ-RAY lines are the most direct probe of cosmic nuclear processes. While it has been recognised[1,2] for two decades that nuclear γ-ray spectroscopy could provide basic information on such problems as solar activity, supernova dynamics and nucleosynthesis, only recently have positive observations of celestial γ-ray lines been made.

The first cosmic γ-ray lines were observed[3] from solar flares. These lines are produced in nuclear processes on time scales of several minutes by the interaction of flare-accelerated particles with the solar atmosphere. Solar γ-ray observations have provided[4] important information on particle acceleration mechanisms, and on the flare process itself.

The strongest observed[5] steady celestial γ-ray line is at 0.511 MeV resulting from positron annihilation. Many mechanisms can contribute to galactic positron production, and two of these, energetic particle reactions and nucleosynthesis, also produce other detectable lines. As we shall show, the bulk of the positrons responsible for this annihilation radiation may come from processes of explosive nucleosynthesis in supernovae. Such positrons result from relatively long-lived radioisotopes whose decay is accompanied by several strong de-excitation γ-ray lines. These lines have not yet been detected, but the predicted fluxes are within the range of instrumentation planned for forthcoming γ-ray observations. The measured 0.511-MeV line intensity already places constraints on the present rate of nucleosynthesis in the Galaxy.

Cosmic γ-ray lines from a transient event have recently been observed[6]. These lines seem to result from energetic particle reactions similar to those that take place in solar flares, but not in similar environments. The identification of the lines requires a redshift of a magnitude that suggests the strong gravitational fields of compact collapsed objects. Such γ-ray line observations may probe nuclear reactions taking place in the vicinity of neutron stars and black holes, and measure the gravitational redshifts of such objects[7].

We first discuss the flare observations and their implications. The study of γ-ray lines from flares is important not only for gaining unique insights into the flare process, but also for the development of the theory of astrophysical γ-ray line production.

* Permanent address: Laboratory for High Energy Astrophysics, Goddard Space Flight Center, Greenbelt, Maryland, 20771.

Solar γ rays

Solar γ-ray lines were first observed[3] from the 4 and 7 August 1972 flares with a NaI(Tl) detector on the 7th Orbiting Solar Observatory (OSO 7). For the 4 August flare, the observed lines, at 2.22, 0.51, 4.44, and 6.13 MeV, and the continuum above 1 MeV, had fluxes of 0.28, 0.06, 0.03, 0.03, and 1 photons cm^{-2} s^{-1} respectively. The duration of the event was about 10^3 s. Lines at 2.22 and 0.51 MeV were also detected during the decay phase of the 7 August flare, but only upper limits could be set on the 4.44 and 6.13 MeV lines and the continuum from this flare. Observations of the 2.2-MeV line have been reported[8,9] from the flares of 22 November 1977 and 11 July 1978.

All these lines result from nuclear interactions of flare-accelerated particles most probably in the chromosphere or lower corona. The strongest line, at 2.223 MeV, is due to neutron capture on hydrogen, $^1H(n, \gamma)^2H$. The neutrons with initial energies of 1–100 MeV, are thermalised and captured in the photosphere. The width of the 2.223-MeV line, determined by the photospheric temperature, is very narrow ($\sim$100 eV). Neutron capure on ^1H, however, must compete[4] with capture on ^3He, even though ^3He is only a minor constituent of the photosphere, because the cross-section for the reaction ^3He (n, p)^3H is about four orders of magnitude larger than that for the reaction ^1H (n, γ)^2H. Observations of the 2.223-MeV line intensity set a limit on the photospheric $^3He/^4He$ ratio of several times 10^{-4}; this limit is comparable to the measured $^3He/^4He$ ratio in the chromosphere and solar wind (see ref. 10).

Radiative neutron capture on ^{56}Fe, which produces two strong lines at 7.632 and 7.646 MeV, is also of considerable astrophysical interest[7]. These lines should be dominant in an iron-rich medium such as the surface of a neutron star.

The second strongest line from solar flares is at 0.511 MeV from positron annihilation. The principal sources of positrons in flares are π^+ mesons, short-lived radioactive positron emitters such as ^{11}C, ^{13}N, ^{14}O and ^{15}O, and the first nuclear level of ^{16}O at 6.052 MeV which decays by electron–positron pair emission. The initial energies of the positrons range from several hundred keV to tens of MeV, but only a small fraction annihilate at these high energies. The bulk of the positrons slow down to energies comparable with those of the ambient electrons, where annihilation takes place either directly or from bound states of

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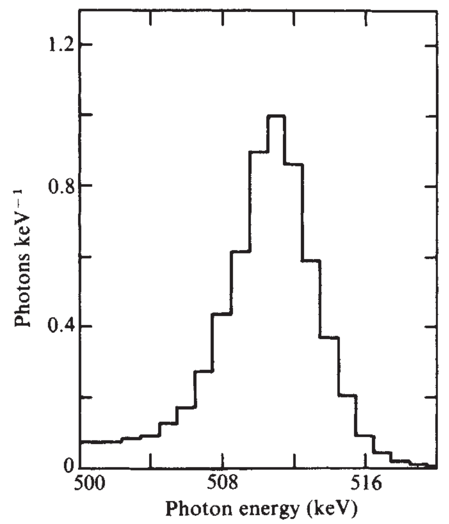

Fig. 1 Calculated[12] spectrum of positron annihilation radiation in cold atomic hydrogen.

positronium. Positronium is formed by radiative combination with free electrons and by charge exchange with neutral hydrogen; 25% of the positronium annihilates from the singlet state and 75% from the triplet state.

Direct annihilation produces two 0.511-MeV photons in the positron–electron rest frame. Singlet positronium also annihilates into two such photons, but triplet positronium decays into three photons which form a continuum at energies below 0.511 MeV. This continuum, however, is significant only if the ambient density is less than about 10^{15} cm^{-3} so that triplet positronium is not broken up by collisions before it can annihilate.

If the ambient medium is almost neutral ($n_e/n_H \leqslant 0.05$), about 95% of the positrons form positronium in flight. If on the other hand, the medium has a higher degree of ionisation, energy loss to the plasma thermalises[11] the positrons before they can annihilate directly or form positronium. In this case, direct annihilation dominates if the temperature is greater than about 10^6 K, while at lower temperatures the positrons form positronium by charge exchange and radiative combination.

If the density of the ambient medium is sufficiently low ($\leqslant 10^{15}$ cm^{-3}), the spectrum of the annihilation radiation in a neutral medium depends on the kinetic energy of the positronium formed in flight and on the positron–neutral atom interaction leading to direct positron annihilation. This spectrum, obtained[12] from a Monte Carlo simulation, is shown in Fig. 1. The full width at half maximum (FWHM) of the 0.511-MeV line is ~5 keV, and the asymmetry due to triplet positronium annihilation can be clearly seen.

In an ionised medium, the width of the 0.511-MeV line depends mostly on the temperature; the FWHM is about 3 keV at 10^5 K and it varies approximately as the square root of the temperature. Note that in an ionised medium the 0.511-MeV line can be substantially narrower than in a neutral medium. For example, in a partially ionised warm gas at 10^4 K (such as in a young supernova remnant) the width of the line is ~1 keV, while in a cold neutral medium (such as an interstellar cloud) the width is ~5 keV.

The expected width of the 0.511-MeV line from solar flares could range[11] from a few keV to several tens of keV depending on whether the annihilation takes place predominantly in the cool photosphere or the hot flare plasma. Because of its low energy resolution, the NaI(Tl) detector on OSO 7 has set only an upper limit (~40 keV), but future high resolution observations, by measuring the line width, may determine the predominant positron annihilation site.

In addition to neutron and positron production, energetic particle reactions lead to many other lines resulting from de-excitation of nuclear levels. Figure 2 shows the spectrum from

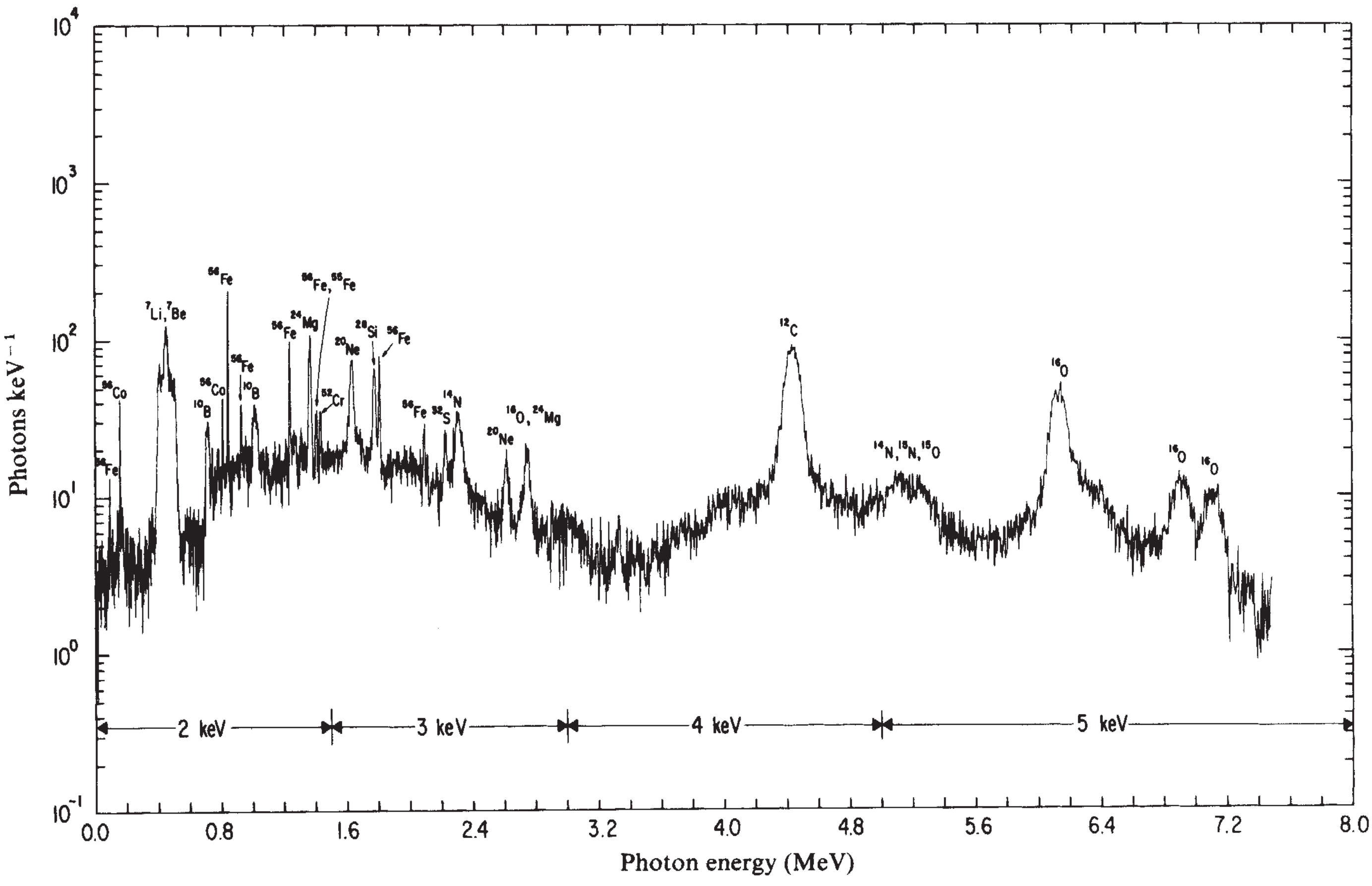

Fig. 2 Calculated[13] nuclear de-excitation γ-ray spectrum from energetic particle reactions.

such de-excitation, calculated[13] by a Monte Carlo simulation of an energetic particle population with spectrum proportional to E^{-2} interacting with a cold ambient medium. Here E is energy per nucleon, and both the energetic particles (at the same E) and the ambient medium are assumed to have solar composition. The narrow lines result from the de-excitation of ambient heavy nuclei excited by energetic protons and α particles, while the underlying broad component is due to de-excitation of energetic heavy nuclei interacting with ambient H and He. The strongest narrow lines, at 4.44 and 6.13 MeV, due to ^{12}C and ^{16}O de-excitation, respectively, were observed[3] from the solar flare of 4 August 1972. Because the ratio of the intensities of the 4.44- and 2.223-MeV lines depends strongly on the spectrum of the energetic particles, the observed ratio provides information on this spectrum in the flare region[4]. The broad component, as well as other narrow lines which were not resolved in the 4 August 1972 observations, could account[14,15] for all of the observed radiation above 4 MeV. Several other narrow lines could also be detected from large flares with instrumentation of higher sensitivity than that flown on OSO 7, for example, the 0.847-MeV line (Fig. 2) from ^{56}Fe and the 15.11-MeV line[16] from ^{12}C.

An important result[10] of solar γ-ray studies concerns the acceleration of protons, nuclei and electrons to energies greater than about 1 MeV. It seems that the mechanism for this acceleration differs from the bulk energisation of solar electrons to tens of keV where they are manifest in powerful hard X-ray emission. Acceleration to higher energies ($\gtrsim$1 MeV), on the other hand, is probably due to a stochastic Fermi-type process which imparts ~1% of the flare energy to a small fraction of the ambient particles. This acceleration may be similar to galactic cosmic-ray acceleration, as several of the properties of the energetic solar particles, such as chemical composition and proton-to-electron ratio, resemble those of the cosmic rays.

Steady galactic γ-ray lines

The best observed[5,17] nontransient galactic γ-ray line is at 0.511 MeV from the galactic centre. The observed[5] line at 510.7±0.5 keV has an intensity of 1.2×10^{-3} photons cm^{-2} s^{-1} and FWHM <3.2 keV. This observation was made in 1977 with a balloon-borne high purity Ge detector of opening angle 15° centred on the galactic centre. The line energy clearly identifies it as positron annihilation radiation; there is also some evidence for the three-photon continuum from triplet positronium annihilation.

The observed spectrum[5] is shown in Fig. 3; the solid curve is the sum of the extrapolated low energy continuum (dashed curve) and a three-photon continuum assuming ~90% annihilation by positronium. This fraction is consistent with positron annihilation in a low density ($<10^{15}$ cm^{-3}) and low temperature ($<10^6$ K) medium[12], and implies about 0.6 photons in the 0.511-MeV line per positron.

The 3.2-keV upper limit on the width of the 0.511-MeV line suggests[12] that the bulk of the positrons annihilate in an ionised medium ($n_e/n_H \gtrsim 0.05$), because in cold interstellar clouds, the line width (~5 keV, Fig. 1) would exceed the observed upper limit. Possible sites of annihilation could be supernova remnants, H II regions at the galactic centre and the warm ionised component of the interstellar medium. Observations with higher spatial resolution could help determine the nature of source.

Turning now to the origin of the positrons, we first consider π^+ mesons produced in high energy (>100 MeV) cosmic ray interactions in the interstellar medium. The π^+ mesons, produced in proton–proton and proton–helium interactions, decay through μ^+ mesons into positrons. An upper limit on this positron source can be set from high-energy (>100 MeV) γ-ray observations[18], as at least part of these γ rays should result from the decay of π^0 mesons which are also produced in the above interactions. From the measured π^+ and π^0 production cross sections, we find that the observed[18] flux (~3×10^{-5} photons cm^{-2} s^{-1}) of >100 MeV γ rays from a 15° cone centred on the galactic centre implies that not more than about 2% of the observed[5] 0.511-MeV line can be from the annihilation of positrons from π^+ decay.

There is probably also a distinct low-energy (<100 MeV) cosmic-ray component; the interstellar density of this component, however, is not known because solar modulation excludes the bulk of the low-energy particles from the inner Solar System. γ-Ray line production from these cosmic rays has been recently evaluated[13] under the assumption that their local interstellar density is 1 eV cm^{-3}, and that there are substantial gradients along the line of sight towards the galactic centre in both the cosmic-ray energy density and heavy element abundances. The resultant γ-ray line emission, including the 0.511-MeV line shown in Fig. 4, is close to its maximal allowed value. If the cosmic-ray intensity were increased, X-ray line emission at ~6.8 keV due to charge exchange of fast Fe ions with interstellar matter would exceed the observational upper limit on this line, and if the heavy element abundances along the line of sight were increased, the absorption of X-rays would be larger than observed. The 0.511-MeV line intensity from low-energy cosmic rays, therefore, should not be larger than $\sim7\times10^{-5}$ photons cm^{-2} s^{-1} rad^{-1}, or also about 2% of the observed line intensity in a 15° cone around the galactic centre.

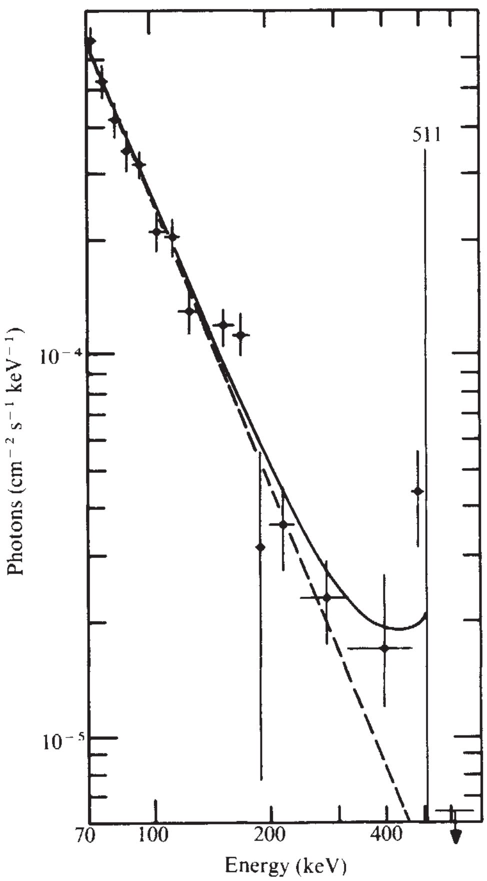

Fig. 3 Observed[5] 0.511-MeV line and low-energy γ-ray spectrum from the galactic centre.

Low-energy cosmic-ray interactions in the interstellar medium, nevertheless, produce a rich γ-ray spectrum which includes many nuclear de-excitation lines, as can be seen in Fig. 4. Of special interest are the very narrow lines, such as that at 6.129 MeV from ^{16}O, resulting from de-excitation of nuclei in interstellar grains[19]. The line broadening, which in gases is caused by the recoil velocities of the excited nuclei, is greatly reduced in solids where these nuclei or their radioactive progenitors can come to rest before de-excitation. The detection of γ-ray lines from low-energy cosmic-ray interactions in the interstellar medium with forthcoming instrumentation would not only measure the unknown interstellar density of these cosmic rays, but also provide unique information on the distribution, motion, composition and size of interstellar dust grains.

Returning to the question of the origin of the positrons, energetic particle reactions at low energies (<100 MeV) could produce positrons in discrete sources (such as in the vicinity of a massive black hole at the galactic centre[7]) without violating the constraints set by the X-ray observations[13]. If this is the case, the 0.511-MeV line should be accompanied by strong broad line emission from nuclear de-excitation, in particular the 4.44-MeV line from ^{12}C. This line may have been observed[17] in 1974 with a balloon-borne NaI (Tl) detector, but this measurement was not confirmed by recent observations (J. L. Matteson, personal communication) with the first High Energy Astronomical Observatory (HEAO 1). The discrepancy could be due to time variations which will be further explored with this and forthcoming satellite-borne γ-ray spectrometers.

If, however, the nuclear interaction rate is essentially constant over the positron annihilation time, then the HEAO 1 upper limit on the 4.44-MeV line intensity from the galactic centre would require that not more than about 30% of the observed 0.511-MeV line result from such energetic particle reactions. This conclusion is only weakly dependent on the assumed composition of the ambient medium and the energetic particles, since the major contributors to positron production, C, N, and O, also produce 4.44-MeV line emission by either direct excitation or spallation. The energetic particle spectrum also does not greatly affect the positron-to-4.4-MeV photon ratio[13]. Thus, some other galactic positron sources may also be required to account for the observed 0.511-MeV line.

One such source[2,20,21] could be relatively long-lived positron-emitting radioisotopes produced by nucleosynthesis during the explosive ejection of matter in supernova explosions. The decay of these isotopes is accompanied by de-excitation γ-ray lines. The principal isotopic decay chains are shown in Table 1, together with the relevant mean lives, de-excitation line energies, and number of positrons and photons per disintegration. The isotopic yields, normalised to ^{56}Ni, are based on Solar System abundances[24], and on the assumption[22,23,25] that all of the Solar System ^{56}Fe, ^{57}Fe and ^{44}Ca, and 1%, 0.5%, and 0.1% of the ^{60}Ni, ^{22}Ne and ^{26}Mg, respectively, are produced explosively through the decay chains shown in Table 1.

Even though nucleosynthesis takes place in dense regions which are opaque to γ rays, the expanding envelope can become transparent if there is sufficient delay between the synthesis of the isotopes and the emission of the photons. For the de-excitation lines, the delay is due only to the lifetime of the parent isotope. But for the 0.511-MeV line, the delay can be longer because of the finite duration of positron slowing down and annihilation. Thus, even relatively short-lived isotopes such as ^{56}Co may be important sources of positrons for annihilation radiation.

Although the lifetime of ^{56}Co may not be long enough for the supernova to become transparent to its de-excitation lines, a significant fraction of the positrons from ^{56}Co may escape from the supernova[20] and annihilate in regions which are transparent to the γ rays. Furthermore, even if transparency is achieved by sufficiently rapid expansion of the supernova envelope and low ejected mass, the de-excitation lines from ^{56}Co decay could only be seen for a short time (a few years) after the explosion. Therefore, these lines would be observable mostly from extragalactic supernovae from which the expected fluxes are relatively small. The slowing down and annihilation times of the positrons, however, can be longer than the interval between supernova explosions[21], and this could lead to an essentially steady galactic emission at 0.511 MeV. The time dependences and detectability of the various other de-excitation lines listed in Table 1 have been discussed in detail elsewhere[23].

Table 1 Isotopic decay chains from nucleosynthesis in supernovae

Decay chain	Mean life (yr)	$Q/Q(^{56}Ni)$	Positrons or photons per disintegration	
$^{56}Ni \rightarrow {}^{56}Co \rightarrow {}^{56}Fe$	0.31	1	e^+	0.2
			0.847 MeV	1
			1.238 MeV	0.7
$^{57}Co \rightarrow {}^{57}Fe$	1.1	2×10^{-2}	0.122 MeV	0.88
			0.014 MeV	0.88
$^{22}Na \rightarrow {}^{22}Ne$	3.8	5×10^{-3}	e^+	0.9
			1.275 MeV	1
$^{44}Ti \rightarrow {}^{44}Sc \rightarrow {}^{44}Ca$	68	2×10^{-3}	e^+	0.94
			1.156 MeV	1
			0.078 MeV	1
			0.068 MeV	1
$^{60}Fe \rightarrow {}^{60}Co \rightarrow {}^{60}Ni$	4.3×10^5	1.5×10^{-4}	1.332 MeV	1
			1.173 MeV	1
			0.059 MeV	1
$^{26}Al \rightarrow {}^{26}Mg$	1.1×10^6	1.5×10^{-4}	e^+	0.85
			1.809 MeV	1

It has been estimated[20] that ~10% of the positrons from ^{56}Co decay could escape from the supernova. This escape fraction would make ^{56}Co the dominant positron source for processes of nucleosynthesis, as can be seen from Table 1. The production of $\sim2\times10^{43}$ positrons s^{-1} in the Galaxy, as indicated by the 0.511-MeV line observations[5], implies a present rate of nucleosynthesis of $\sim10^{45}$ iron nuclei s^{-1}. This is ~10% of the average rate of nucleosynthesis over the age of the Galaxy, and is consistent with current models[26] of galactic chemical evolution. The fraction of escaping positrons from supernovae is very uncertain, however, and requires further theoretical study. If the escape fraction for ^{56}Co were much lower than 0.1, ^{22}Na decay could become the dominant positron source, as can be seen from Table 1. But the ^{22}Na yield from supernovae[25] is also very uncertain. ^{22}Na is also produced in novae, with a yield of about 10^{48} nuclei per nova explosion[27]. To produce $\sim2\times10^{43}$ positrons s^{-1} in the Galaxy, however, ~600 novae per year would be required, and this rate is higher by an order than current estimates of the galactic nova rate.

As there are other potential positron sources, a test of the explosive nucleosynthetic origin would be the detection of the associated de-excitation γ-ray lines. A good prospect is the 1.809-MeV line from ^{26}Al decay[28]. Because of the long lifetime of this isotope, the 1.809-MeV line should be observed as steady galactic emission with an intensity of $\sim5\times10^{-5}$ photons cm^{-2} s^{-1} rad^{-1} from the direction of the galactic centre; the long half-life of the ^{26}Al also implies a very narrow width for this line (~3 keV).

Another possible positron source could be pair production in the magnetosphere of pulsars[29]. But observations of the Crab Nebula have so far not detected line emission at 0.511 MeV from this object. Although a line at 0.400 MeV, attributed to gravitationally redshifted 0.511-MeV emission was detected[30] from the general direction of the Crab, this line was not seen[6] in an earlier flight which viewed the same region. This suggests that the 0.400-MeV line from the direction of the Crab could be due to a transient event.

Transient γ-ray lines

In addition to steady γ-ray line emission exemplified by the 0.511-MeV line from the galactic centre, γ-ray lines have also been observed from transient events. γ-Ray bursts of duration up to tens of seconds are a well recognised cosmic phenomenon, but their energy spectra have not yet been measured with sufficient resolution to discern whether they contain significant line emission. There seems, however, to be another class of

γ-ray transients in which essentially all the observed radiation is in the form of lines. Such a γ-ray line transient was discovered[6] with a balloon borne Ge(Li) detector on 10 June 1974. This event, lasting ~20 min was characterised by strong emission in four relatively narrow energy bands or lines with no detectable continuum. The four observed lines at energies of 0.40–0.42, 1.74–1.86, 2.18–2.26 and 5.94–5.96 MeV had average intensities of 7×10^{-3}, 3.2×10^{-2}, 1.5×10^{-2} and 1.5×10^{-2} photons cm^{-2} s^{-1}, respectively, during the event. These lines showed statistically significant increases in emission compared both to the intensity in the adjacent continuum and to that in the same energy bands before and after this event. A simultaneous increase was observed in the CsI(Na) shield detectors with an intensity consistent with that observed just in the lines. This transient source seems to lie within ~20° of RA 7h and dec 20°. One possible candidate for the source is the object γ195+5 which has been observed[31] in high-energy γ rays but not yet at other wavelengths. The Crab Nebula was also near the edge of the field of view.

There are no simple nuclear schemes that can account for all four observed lines, as there are no obvious candidate nuclei for direct emission at ~0.41 and 5.95 MeV. A source seems to be required[7] which is effectively bimodal, producing both redshifted and non-redshifted lines. The observations could then be understood in terms of neutron capture and positron annihilation, which are also the strongest line producing mechanisms in solar flares. Specifically, the ~0.41-MeV line could be redshifted positron annihilation radiation and the 1.79- and 5.95-MeV lines could be redshifted neutron capture on ^1H and ^{56}Fe, respectively. The required redshift Z of between 0.24 and 0.28, could arise from the gravitational field of a neutron star of mass 1.4–1.8 M_0. Episodic accretion onto such a neutron star from a close binary companion could lead to the formation of a high temperature (>10^{10} K for ions) accretion disk in which nuclear interactions could take place producing neutrons and positrons. Positron annihilation and neutron capture on iron and hydrogen at and near the surface of the neutron star would produce the observed redshifted line emission, while the same processes in the accretion disk and in the atmosphere of the companion star would produce essentially unshifted lines, of which only the 2.223-MeV line from neutron capture on hydrogen was observed. The unshifted 0.511-MeV positron annihilation line was not seen because of the large atmospheric and detector background at this energy. The double line from neutron capture on iron should be significant only in the redshifted emission from the iron-rich surface of the neutron star but not in the unshifted emission.

As mentioned above, the 0.400-MeV line observed[30] in May 1976 from the general direction of the Crab Nebula may also have been a γ-ray line transient as it was not detected[6] in an earlier flight. The June 1974 and May 1976 events may in fact have the same source, as both observations included much of the same field of view; the latter event, however, was weaker by a factor of 3.

Extragalactic γ-ray lines

γ-ray lines at 4.4 and 1.6 MeV have been reported[32] from the radiogalaxy Centaurus A. The 0.511-MeV line, however, which is so prominent in the spectra of solar flares and the galactic centre, was not observed from Cen A. If the γ-ray lines from Cen A are produced[7] in quasithermonuclear reactions in the vicinity of a massive black hole[33], then the absence of the 0.511-MeV line could be due to the large Doppler broadening in the hot accretion gas which would make the line unobservable above the continuum. γ Rays in the MeV region have also been reported[34] from the Seyfert galaxy NGC4151, but the energy resolution was not sufficient to resolve possible line emission.

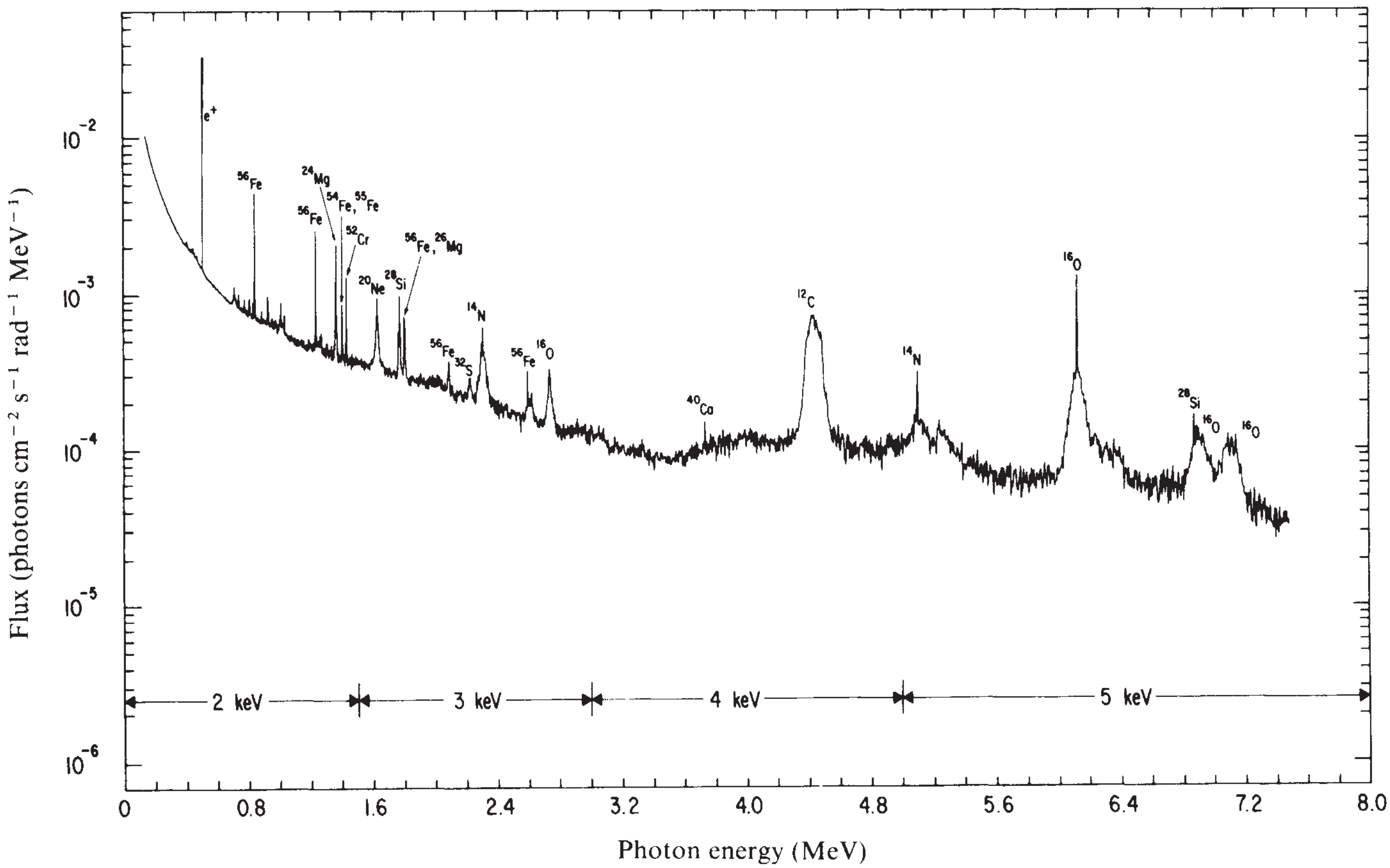

Fig. 4. Expected[13] γ-ray spectrum from low-energy cosmic-ray interactions in the galaxy in the general direction of the galactic centre.

Outlook

Information on many astrophysical process and sites is encoded in the γ-ray line observations reviewed here. Following these exciting discoveries, γ-ray line astronomy is now moving into an era of more systematic study, made possible by the launch of HEAO 1 and the anticipated launches of HEAO C and the Solar Maximum Mission (SMM) in the autumn of 1979. The γ-ray spectrometer on HEAO 1 is already giving results. Within a year, solar flares will be explored with the γ-ray spectrometer[35] on SMM, and galactic and extragalactic γ-ray lines will be studied by a high resolution spectrometer[36] on HEAO C. At the same time, high altitude balloon-borne spectrometers should continue to provide important results on discrete sources.

Looking further into the future, perhaps the most exciting prospect for γ-ray line astronomy will come with the launch of the Gamma Ray Observatory in 1984. This observatory is not yet an approved mission. Two of its five experiments, a Ge spectrometer and a NaI spectrometer, will observe γ-ray lines with much higher sensitivities than the instruments flown to date or planned for the immediate future. Together, these satellite and balloon-borne experiments should establish γ-ray line astronomy as a vigorous observational science.

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articles

Water–rock partition coefficients and the composition of seawater and river water

M. Whitfield & D. R. Turner

Marine Biological Association of the United Kingdom, The Laboratory, Citadel Hill, Plymouth, UK

Using a simple chemical reactor model a strong correlation is established between the mean oceanic residence time of an element and the partitioning of that element between seawater and crustal rock. The ocean-rock partition coefficient ($K_{Y(sw)}$) is shown to be related to the electrostatic contribution to the element–oxygen bond energy (Q_{YO}) and a second correlation is established between these parameters. In this way the concentrations of all the elements so far identified in seawater fall in a coherent pattern. The global mean composition of river water, which represents an intermediate step in the formation of seawater from rock weathering, is shown to conform to a similar pattern.

THE concentrations of nearly 70 elements have now been determined in seawater and, although the chemistry of seawater has been frequently reviewed[1–3] no general rules have emerged that enable the concentrations of all the elements to be incorporated in a simple yet coherent pattern. According to one hypothesis[4–6], seawater has been produced by the reaction,

$$\text{Igneous rocks} + \text{Acid volatiles} + \text{Water} \rightarrow \text{Seawater} + \text{Sediment} + \text{Atmosphere}$$

As there have been no major changes in the mean composition of either the igneous rocks or the sediments over the past few billion years[4,7] the composition of seawater has probably remained fairly constant over this period—in order of magnitude terms at least. Aided by the vast flux of material through the oceans[5,7] and by the uplift and reweathering of sedimentary rock[7,8] (sometimes following metamorphosis) the ocean–rock

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