

EVALUATION OF EARTH'S GEOBIOSPHERE EMERGY BASELINE AND THE
EMERGY OF CRUSTAL CYCLING

By

CHRIS DE VILBISS

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To myself first and foremost and secondarily to my family, mom, dad, sister, grandparents, and to my advisor Dr. Brown and to all who support me and my passions and dreams

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LIST OF ABBREVIATIONS

Ga	Giga-annum, i.e. one billion years
GEB	Geobiosphere energy baseline
Gej	Gravitational emjoule
GPE	Gravitational Potential Energy
ME	Mass enrichment method
NEAD	National Energy Accounting Database
RE	Reference environment
Sej	Solar emjoule
seJ	Solar equivalent Joule
SER	Solar Equivalence Ratio
UEV	Unit Energy Value

Abstract of Dissertation Presented to the Graduate School
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By

Christopher Daniel De Vilbiss

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This dissertation quantitatively analyzed the exergy supporting the nucleosynthesis of the heavy isotopes, Earth's geobiosphere, and its crustal cycling. Exergy is that portion of energy that is available to drive work. The exergy sources that drive the geobiosphere are sunlight, Earth's rotational kinetic energy and relic heat, and radionuclides in Earth's interior. These four exergy sources were used to compute the Earth's geobiosphere emergy baseline (GEB), expressed as a single unit, solar equivalent joules (seJ).

The seJ of radionuclides were computed by determining the quantity of gravitational exergy that dissipated in the production of both sunlight and heavy isotopes. This is a new method of computing solar equivalences also was applied to Earth's relic heat and rotational energy. The equivalent quantities of these four exergy sources were then added to express the GEB. This new baseline was compared with several other contemporary GEB methods.

The new GEB is modeled as the support to Earth's crustal cycle and ultimately to the economical mineral deposits used in the US economy. Given the average annual

cycling of crustal material and its average composition, specific emergies were calculated to express the average energy per mass of particular crustal minerals. Chemical exergies of the minerals were used to develop transformities and specific emergies of minerals at heightened concentrations, i.e. minable concentrations. The effect of these new mineral energy values were examined using the US economy as an example. The final result is an 83% reduction in the emergy of limestone, a 91% reduction in the aggregated emergy of all other minerals, and a 23% reduction in the emergy of the US economy.

This dissertation explored three unique and innovative methods to compute the emergy of Earth's exergy sources and resources. First was a method for computing the emergy of radionuclides. Second was a method to evaluate the Earth's relic heat and dissipation of gravitational exergy that uses forward computation. Third is a more consistent method to compute the emergy value of crustal minerals based on their chemical exergy.

CHAPTER 1 INTRODUCTION

Emergy is a quantitative measure of nature's work that can help guide political and economic decisions. To guide these decisions preliminary indicators were developed for the major resources of the Earth (e.g. minerals, fossil fuels, lumber, renewable energies such as rain, wind, sunlight, etc.). Over time some of these original indicators continue to be used, while others are updated to new scientific data or new methods. To be comprehensive, some indicators were developed for resources without energetic basis. Hence sometimes researches may use outdated or inappropriate indicators. The improvement of such indicators is a major impetus of this dissertation.

The greatest utility of the emergy method is its single, common unit of measure which can evaluate and compare all products and processes. Using a system's perspective researchers compile pertinent components of systems into models with accompanying inflows, outflows, internal loops, storages, and interactions. Too much detail makes the models intractable, too little detail makes the results overly general. Thus generalizations, aggregations, and assumptions are made. Many of these assumptions regarding the computation of the global emergy baseline and the emergy of the crustal system are questioned and modified in this dissertation.

To begin we should define emergy. Emergy is the dissipated potential energy of one form, from a pre-defined time origin, needed to produce a given system under consideration (Giannantoni, 2002 after Odum, 1996). The utility of expressing various forms of potential energy (hereafter referred to as exergy¹) in a single unit is analogous

¹ Exergy means *available potential energy*. Exergy is "the amount of work obtainable when some matter is brought to thermodynamic equilibrium with the common components of the natural surroundings by

to expressing different forms of currency in a single currency via an exchange rate. Only the common unit can be used for comparison, see for example oil equivalents for various fossil fuel sources. In the modern energy community, energy is expressed as solar emjoules, different from a solar equivalent joule (explained later).

The upstream resource and energy demands of a process is accounted to assess its environmental support. If one traces far enough upstream all of Earth's resource generation processes, eventually one comes to the sources of energy to the planet, the sunlight, deep earth heat, and ocean tides. These three sources (or four as discussed later) are independent of each other and interact to produce all the indigenous resources used by ecosystems and modern societies. The sum of the energy of these planetary sources is called the geobiosphere energy baseline (GEB).

Originally this dissertation aimed to reevaluate the energy of crustal minerals. The impetus for researching crustal minerals came from the fact that globally, human used crustal mineral energy rivaled the GEB in magnitude and yet the methods to compute mineral energy were perhaps the most vague of all energy methods. During the reevaluation of mineral energy, whose genesis time is billions of years, deep research into the geodynamic history of the Earth revealed knowledge that could be used to re-evaluate the GEB. Thus, the process of evaluating crustal mineral energy spawned the re-evaluation of the GEB.

One new geodynamic understanding was that radiogenic heat deep in the Earth is independent to relic heat that remains from Earth's accretion. In previous studies, the radiogenic component of deep heat was assumed to have the same transformity as

means of reversible processes, involving interaction only with the above-mentioned components of nature" (Szargut et al., 1988).

accretion heat. This assumption was due to the up until now inability to compute the solar equivalence of radioactive isotopes in the Earth's crust.

Chapter 2 of this document uses gravity as the primary input to both sunlight and heavy radionuclides and computes their gravitational transformities (an exergy conversion/transformation ratio). We then compute solar equivalence ratios (SERs) between sunlight and the four major crustal radionuclides (^{238}U , ^{235}U , ^{232}Th , ^{40}K). These SERs are used to express the solar equivalent exergy of the radiogenic component of geothermal heat flow. Similarly the tides and primordial geothermal heat can be quantified in terms of the gravitational exergy required to produce them, which is the subject of Chapter 3.

Several novelties come from Chapter 2, which were published (Siegel et al., 2016). First, the radiogenic component of deep heat is separate from, and of a different quality than primordial accretion heat. Second, the four energy sources to the geobiosphere are not transformations of Sunlight and are in fact independent of each other. Thus solar transformities (defined as the solar energy per unit exergy) is not an appropriate indicator of their quality and so we develop solar equivalent ratios (SERs). And third, there are in fact four independent sources to the geo-biosphere, solar radiation, primordial heat, radiogenic heat and tidal dissipation.

In Chapter 3 we expand the knowledge from Chapter 2 to re-evaluate the emergy of all four independent sources of energy to the geo-biosphere. In the method of Chapter 3 we consider gravitational potential energy (GPE) the common source to all of Earth's energy sources. From this gravitational perspective, we recognize three refinements to our understanding of Earth's driving energies. First we acknowledge that

Earth's geothermal energy is from two separate sources, decay of radioisotopes and primordial heat, and each require a unique UEV. Second, tidal energy is the dissipation of Earth's rotational kinetic energy (KE). Earth/Moon/Sun interact to drag the oceans on their basins and shelves causing frictional dissipation known as tides. Seen this way we equate the loss of Earth rotational KE and tidal energy dissipated. Third, Earth's rotational KE and primordial heat are coupled products of the gravitationally induced accretion of Earth. We are not able to definitely describe these coupled products as splits, co-products, or by-products, and therefore we compare the merits of each.

The four exergy sources to geobiosphere are expressed as a ratio of gravitational emergy needed to produce them to their exergy content. This is a gravitational transformity. Each planetary source has a solar equivalence according to the ratio of their gravitational transformity to the gravitational transformity of sunlight. These solar equivalence ratios are combined to express a single quantity, the GEB, which is $13.9 \text{ E}24 \text{ seJ J}^{-1}$. This value is similar to baselines computed using other methods (Brown and Ulgiati, 2016; and Campbell, 2016).

Using our new GEB we reevaluate the crustal mineral emergy in Chapter 4. Crustal genesis occurs over billions of years (the time scale of the GEB). To date, unit emergy values (UEVs) for crustal minerals (e.g. limestone, iron ore, etc.) have lacked a thermodynamic basis. Here, we will assume a steady state crustal cycle that embodies the GEB and find the UEV of average crust to be $1.38 \text{ E}9$ solar emjoules per gram (specific emergy). The ratio of crustal specific emergy to its exergy density (exergy per mass) is the mineral's transformity. This is an important assertion as it is the dissipation of exergy that hierarchically organizes materials (Odum, 2001). Perhaps the most

significant contribution of Chapter 4 is the affirmation that all resources that have energy can be expressed as both a transformity and specific energy. This assertion had yet to be made and without which made possible the previously more vague descriptions of mineral energy. Transformity and specific energy are linked by exergy density and every resource which possesses potential energy (exergy), and therefore possesses energy, has all three. It must be possible to express every resource, including crustal minerals, as either a transformity or specific energy in order to be theoretically consistent with energy's thermodynamic basis, even if we only use one or the other.

Six potential methods for quantifying mineral transformity are discussed in detail Chapter 4. In summary, here, mineral transformity can be characterized using either a crustal average transformity, or unique mineral chemical exergy transformities or Gibb's formation energy transformities. All three can be accounted using their total exergy, or just their mixing term, the latter of which depends on average crustal abundance of the mineral. These six proposed methods yield a wide range of specific energies. We conclude that the exergy of concentration (mixing exergy) using transformities derived from Gibb's formation energy better suit the energy method because chemical exergy transformities do not yield the presupposed correlation between abundance and mineral specific energy, whereas Gibb's transformities and average crustal chemical exergy transformity does. However, average crustal chemical exergy transformity is equivalent for all minerals, which ignores the uniqueness in each mineral species. The energy accounting of minerals should utilize Gibb's transformities and account only the energy of a mineral's mixing exergy because this represents the natural capital that is destroyed in mineral harvesting.

In summary, this dissertation reevaluates the emergy of each exergy source to the geobiosphere and of the crustal minerals. The new number reduces the magnitude of the GEB by about 10% from its previous $15.2 \text{ E}24 \text{ seJ yr}^{-1}$ (Brown and Ulgiati, 2010) to $13.9 \text{ E}24 \text{ seJ yr}^{-1}$. This alone has implications for the crustal mineral emergy which comprised about 26% of the emergy of the US economy in 2008. 90% of this 26% comes from the emergy of limestone. We reevaluate the emergy of limestone as a biogenic resource, whereas up until now it was evaluated as a crustal resource. The new crustal mineral emergy values overall reduce the contribution of mineral emergy to the US economy from about 26% of the total to 5.8%. These results come from the link we created between transformity and specific emergy for minerals, a link which had yet to exist.

CHAPTER 2 CALCULATING SOLAR EQUIVALENCE RATIOS OF THE FOUR MAJOR HEAT- PRODUCING RADIOGENIC ISOTOPES IN THE EARTH'S CRUST AND MANTLE

Emergy of Radionuclides

Radionuclides are atoms which emit ionizing radiation. They contribute to modern economies in various ways from food preservation, biochemistry, geology, nuclear medicine, and power generation systems. Radionuclides also contribute a substantial portion of heat to Earth's internal heat flow. These radioactive atoms are mined economically when their mineral abundance in Earth's crust justifies their extraction. However nuclear exergy is not captured simply by mineral abundance. The majority of crustal mineral inputs to human systems are considered as contributions of chemical exergy. Their unit emergy values (UEVs)¹ are computed using the product of average crust specific emergy ($1.38 \text{ E9 sej g}^{-1}$) to the mineral's Gibbs mixing exergy at its mine abundance in the crust (Chapter 4). The radionuclides, however are used for their nuclear exergy and evaluations based solely on their abundance in the crust miss this nuclear contribution. In Chapter 2 we evaluate the gravitational exergy used in nucleosynthesis during stellar fusion reactions to find gravitational transformities and ultimately to compute solar equivalence ratios (SERs) for the four major heat-producing isotopes (^{238}U , ^{235}U , ^{232}Th , ^{40}K) of earth.

The production of light and the synthesis of heavier forms of matter are simultaneous processes, so the resulting solar radiation and heavy elements are co-products. In our Sun proton-proton fusion reactions combine hydrogen nuclei to form

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¹ Abbreviations used in this paper: SER = solar equivalence ratio, sej = solar emjoule, Gej = gravitational emjoule, seJ = solar equivalent Joule, GPE = gravitational potential energy, UEV = unit emergy value. (See Brown and Ulgiati, 2016)

helium. The energies involved in these reactions are well known and are used to compute a solar equivalent exergy of fusion products.

The procedures outlined in this paper differ from previous calculations of solar equivalence of the primary geobiosphere inputs as outlined by Odum (2000). The following section provides an innovative method to forward (causatively) calculate the gravitational energy required to produce the GEB.

Methods

The fusion process requires gravitational exergy as a catalyzing input. The two co-products, solar radiation and heavier elements can be expressed in terms of gravitational energy (expressed as gravitational emjoules or gej)². Gej is the amount of gravitational exergy required in the steps of the fusion reactions. The result is two gravitational transformities, one for solar exergy and one for radiogenic exergy. The gravitational transformity of radiogenic exergy ($\varphi\tau_R$; *units = gej/J*), and the gravitational transformity of Sunlight ($\varphi\tau_S$; *units = gej/J*) can be used to compute a solar equivalence ratio (SER) between Sunlight and radiogenic exergy (Eq. (2-1)):

$$\frac{\varphi\tau_R}{\varphi\tau_S} = SER \quad (2-1)$$

The units of which are $gej/(J_{\text{Radiogenic}})/(gej/J_{\text{Sunlight}}) = J_{\text{Sunlight}}/(J_{\text{Radiogenic}})$

The exergy of 1 atom of radionuclide is known (the energy released through radioactive decay) and thus the solar equivalence ratio (SER) of radiogenic exergy is

² According to the definition of emergy (cumulative exergy of one form required directly or indirectly to support a process), we introduce in this paper a new unit of emergy, gravitational emergy, defined as the cumulative gravitational exergy required to support Earth's elementary exergy sources (i.e. Sunlight, matter, rotational kinetic energy, and heat). As a consequence, we also define a gravitational transformity for Sunlight and radiogenic exergies (τ_S and τ_R) respectively.

solar equivalent joules per joule of heat released (seJ J^{-1}). The SER is not a transformity (sej/J).

Gravitational exergy used in the production of solar radiation is the numerator (the energy) for $\phi \tau_S$, and the gravitational exergy used in heavy element nucleosynthesis in supernova stars many times more massive than the Sun is the numerator $\phi \tau_R$. We assume gravity equal everywhere. That is, the gravitational exergy used to make sunlight has equal quality (universally speaking) to gravitational exergy used in heavy element nucleosynthesis.

We use thermal energy as a proxy for gravitational exergy required in nuclear fusion. We rationally that gravitational exergy is translated into thermal energy by increasing the total pressure of the plasma gas inside stars. This thermal kinetic energy is the operative energy at the locality of fusion reactions, and results in collisions that enable nuclear processes to occur. Considering a cosmic scale of the universe, we generalize that thermal energy is always precipitated by gravity because increases in temperature require a concentration of particles, and gravity is the only effective force at this scale. Approximate average temperatures at which our fusion reactions occur, both in the Sun and in supernova, are known and can be translated directly into estimates of thermal energies.

Thermal energy is defined as the average translational kinetic energy possessed by free particles according to the theorem of equipartition of energy, which states that particles in thermal equilibrium will have the same average kinetic energy associated with each independent vector of motion. The average translational kinetic energy of a plasma is the expected value of the kinetic energy where the expected velocities of

plasma particles follow a Maxwell-Boltzmann distribution (Eq. (2-2)) where k_B is the Boltzmann constant equal to 1.38×10^{-23} J/K.

$$\langle E_{ke} \rangle = \frac{1}{2} m \langle v^2 \rangle = \frac{1}{2} m \int_0^\infty v^2 \frac{4}{\sqrt{\pi}} \left(\frac{m}{2k_B T} \right)^{2/3} v^2 dv e^{-mv^2/2k_B T} = \quad (2-2)$$

$\frac{3}{2} k_B T N$ where $N = 2$ is the number of particles per reaction

A special case involves assessing the thermal energies associated with type II supernova explosions. The tremendous energies released in these events are catalyzed by gravitational collapse of large iron core (which must exceed the Chandrasekhar limit of 1.4 solar masses) of a star into a very dense and hot neutron core. This collapse is very low entropy (Bethe, et al 1979), and after several milliseconds the core itself resembles a macroscopic nucleus and is effectively incompressible. The gravitational energy of collapse is then rebounded into a shock wave that immediately precipitates r-process nucleosynthesis, responsible for the heaviest isotopes in the universe. Among these are U^{235} , U^{238} , and Th^{232} - three of the four major radionuclides generating geothermal heat in the earth. The fourth, ^{40}K , is formed in explosive oxygen-burning process, also ignited by type II supernova (Shimansky et al., 2003).

Results and Discussion

Gravitational Energy of Solar Radiation

Solar radiation is the result of two fusion cycles (known as the PPI and the PPII chains) inside the Sun. The PPI chain (shown in Figure 2-1) is a set of three reactions that fuse 4 protons into one helium atom, in the process releasing about 26.2 MeV of solar radiation, plus some neutrino energy. The PPII chain (shown in Figure 2-2) is a set of six reactions that fuse four protons and one 4He atom into two 4He atoms, and involves the burning of beryllium and lithium-7, yielding 51.807 MeV (Clayton, 1968).

The reactions of the chains and the associated radiative outputs of each reaction are given in Tables 2-1 and 2-2 where solar output for each reaction is taken from the literature.

To compute the gravitational energy required to produce sunlight we use the temperatures at which these two fusion reactions occur. Because the Sun's core burns at 15.7×10^6 K (Ryan and Norton, 2010), the gravitational input for each reaction in the PPI cycle can be computed using Eq. (2-2).

$$((3k_B(15.7 \text{ E6 K})/2) * 2 \text{ particles per nuclear reaction} = 6.50 \text{ E-16 J}$$

The gravitational energy in the final row of Tables 2-1 and 2-2 is the sum total of the GPE input for all reactions in these reaction cycles. The frequency of occurrence of the PPI and the PPII chains is 86% and 14% respectively (Clayton, 1968).

Fraction of solar radiation from PPI:

$$= 0.86(26.202 \text{ MeV})/[0.86(26.202 \text{ MeV}) + 0.14(51.807 \text{ MeV})] = 76\%$$

Fraction of solar radiation from PPII:

$$= 0.14(51.807 \text{ MeV})/[0.86(26.202 \text{ MeV}) + 0.14(51.807 \text{ MeV})] = 24\%$$

Gravitational Transformity of Sunlight

The total accumulated gravitational energy divided by the final solar exergy output of each chain yields the gravitational transformity (gej/J_{Sunlight}) for the PPI and PPII chains:

PPI (26.202 MeV total output):

$$3.25E - 15 \text{ gej} / [26.202 \text{ MeV} \times 1.602E - 13 \text{ J/MeV}] = 7.75E - 4 \text{ gej/J sunlight}$$

PPII (51.807 MeV total output):

$$5.85E - 15 \text{ gej} / [51.807 \text{ MeV} \times 1.602E - 13 \text{ J/MeV}] = 7.05E - 4 \text{ gej/J sunlight}$$

These transformities imply that for every input of 0.000775 J (PPI cycle) and 0.000705 J (PPII cycle) of GPE dissipated in the stellar core, 1 J of sunlight is produced (See EndNote 1 for further discussion).

The PPI chain, which generates about 76% of sunlight, has a gravitational transformity of $7.75E-4 \text{ gej/J}_{\text{Sunlight}}$. The PPII chain contributes about 24% to sunlight and has a gravitational transformity of $7.05E-4 \text{ gej/J}_{\text{Sunlight}}$. The weighted average of these two is ${}_{g}\tau_S = 7.65E - 4 \text{ gej/J}$.

Gravitational Energy of Radionuclides

Gravitational transformities for radionuclides were computed similarly as for sunlight. Unlike in our main-sequence Sun, radionuclides are formed primarily through r-process (rapid process) nucleosynthesis in the very high temperatures generated by type II supernova explosions. These supernova temperatures were used to calculate the average energies of reactants in nuclear fusion reactions for each heavy nuclide.

Potassium

Nucleosynthesis of ${}^{40}\text{K}$, the third most significant contributor to radiogenic heat in the Earth's crust and mantle, occurs in two steps (Figure 2-3). The first is the helium burning cycle that occurs post-hydrogen burning in medium and large stellar cores at temperatures around $3 \times 10^8 \text{ K}$ (Meyer et al., 2008). This step generates ${}^{12}\text{C}$ then ${}^{16}\text{O}$, which is the dominant product of the helium burning cycle. ${}^{16}\text{O}$ is the substrate for the next step of ${}^{40}\text{K}$ production, explosive oxygen burning, which occurs during type II supernova at temperatures around $3.5 \times 10^9 \text{ K}$ (Truran and Arnett, 1970). In these

conditions oxygen fuses into sulfur, and sulfur fuses with free alpha particles (helium nuclei) to form calcium-40, which undergoes neutron capture and proton emission to become potassium-40 (Woosley et al., 1973). The overall set of reactions, are shown in Figure 2-3 and summarized in Table 2-3.

Both the helium burning phase and the explosive oxygen burning phase are important contributions to the gravitational energy of ^{40}K . The gravitational energy required per reaction for these two steps (using Eq. (2-2)) corresponds to $(3/2)k_B(3E8\text{ K})(2\text{ particles/reaction}) = 1.24E-14\text{ gej/helium burning reaction}$, and $(3/2)k_B(3.5E9\text{ K})(2\text{ particles/reaction}) = 1.45E-13\text{ gej/oxygen burning reaction}$, respectively. The first reactant, however, is ^4He , for which we have two values for energy/atom (one from the PPI chain, another from PPII). A weighted average of these based on frequency of occurrence in our Sun is $0.86(3.25E-15) + 0.14(5.85E-15) = 3.62E-15\text{ gej}/^4\text{He}$. The third column in Table 2-3 lists the gravitational energy required for each reaction depending on whether it is helium burning ($6.21\text{ E-}15\text{ gej/particle}$) or explosive oxygen burning ($7.25\text{ E-}14\text{ gej/particle}$). The final row of the gravitational energy column is the sum of the gravitational energy of all reactions plus the energy of the ^4He reactants.

The exergy of radioactive decay of ^{40}K is 0.7 MeV (Stacey and Davis, 2008). Using the total gravitational energy ($6.91\text{ E-}13\text{ gej}/^{40}\text{K}$) from Table 2-3, the gravitational transformity for the radioactive decay of ^{40}K is

$$g\tau_{40K} = \frac{6.91\text{ E-}13\text{ gej}}{0.7\text{ MeV} \cdot 1.6\text{ E-}13\text{ J/MeV}} = 6.16\text{ gej/J}_{40K}$$

Heavy radionuclides (^{232}Th , ^{235}U , and ^{238}U)

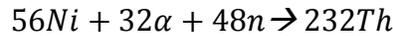
The rare heavy radionuclides (^{232}Th , ^{235}U , and ^{238}U) are the result of r-process nucleosynthesis, which means rapid neutron capture by heavy “seed-nuclei”. To

compute the gravitational energy required to synthesize the heavy radionuclides, not only are the thermal energies of r-process nucleosynthesis necessary (calculated as $1.22\text{E-}13$ J, see EndNote 2), but also the energy of the alpha particles and the seed nuclei must be included. The heaviest and most likely seed nuclei required for uranium and thorium formation is peak iron, which is the stable decay product of ^{56}Ni , and which is the final product of non-explosive nucleosynthesis and signifies the end of stellar fuel (Pagel, 2009). The core collapses and any ^{56}Ni remaining can be seeds for neutron and alpha particle capture in the hot bubble surrounding a fresh supernova.

The energy of seed-nuclei ^{56}Ni is the sum of gravitational energy used for its formation which includes a cascade of reactions at various temperatures during the normal hydrostatic burning stages in presupernova stars (Figure 2-4). Table 2-4 lists the reaction steps and the gravitational energy required to synthesize ^{56}Ni . As shown in the Figure 2-4 there is a necessary input of helium which is shown as the initial input of 3 ^4He atoms per ^{12}C atom, each with a gravitational energy of $3.62\text{ E-}15$ geJ/atom. The helium burning reaction occurs twice, once to create ^8Be , and then ^8Be combined with an alpha particle to become ^{12}C . The required GPE per reaction in this step is (2 particles/reaction)($6.21\text{ E-}15$ J/atom)= $1.24\text{E-}14$ geJ/reaction. The output of the helium burning step is two ^{12}C atoms which have gravitational energy of $3.57\text{E-}14$ geJ/ ^{12}C . In the carbon burning stage two ^{12}C are combined with two ^4He yielding two atoms of ^{16}O ($5.17\text{ E-}14$ geJ/ ^{16}O). The subsequent oxygen-burning stage yields ^{28}Si ($1.66\text{ E-}13$ geJ/ ^{28}Si). When the oxygen fuel is exhausted, the final stage of Si-burning begins, which is actually just a succession of alpha-capture reactions, yielding ^{56}Ni ($9.70\text{ E-}13$ geJ/ ^{56}Ni).

With the gravitational energy required for ^{56}Ni synthesis, gravitational transformities $(g\tau_R)^3$ for the r-process radionuclides can be computed. For each reaction the gravitational exergy used is a function of two colliding particles. In the case of heavy radionuclides which are synthesized during r-process nucleosynthesis during supernova explosions, many successive two particle reactions occur in rapid succession. However each is here considered a separate two particle reaction. In all cases output neutrino energy is excluded from the accumulating gravitational energy of the heavy radionuclide.

The ^{232}Th reaction is as follows, where n denotes neutrons⁴.



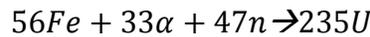
and the energy/atom of thorium is as follows.

$$9.74E - 13 \text{ gej} + 32(3.62E - 15 \text{ gej}) + (32 + 48)[2(1.22E - 13 \text{ gej})] = 2.06E - 11 \text{ gej}$$

The energy released during complete decay of ^{232}Th ($^{232}\text{Th} \rightarrow 6\alpha + 4\beta + ^{208}\text{Pb} + \nu_e$) is 42 MeV, with 1.5 MeV neutrino energy (Stacey and Davis, 2008). The neutrino energy carried is subtracted, as it's unusable, so we have a gravitational transformity for ^{232}Th as follows:

$$g\tau_{232\text{Th}} = \frac{2.06E - 11 \text{ gej}}{40.5 \text{ MeV}} = 3.18 \text{ gej/J}_{232\text{Th}}$$

The ^{235}U reaction,



yields an energy/atom of ^{235}U equal to:

$$9.74E - 13 \text{ gej} + 33(3.6E - 15 \text{ gej}) + (33 + 47)[2(1.22E - 13 \text{ gej})] = 2.06E - 11 \text{ gej}$$

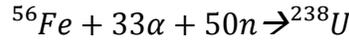
³ Gravitational transformity is abbreviated ($g\tau$) to differentiate it from solar transformities (τ).

⁴ Just as we have considered protons, neutrons carry no gravitational energy. They are considered primordial matter. A reference state of zero gravitational energy per neutron is assumed.

The energy released during complete decay of ^{235}U ($^{235}\text{U} \rightarrow 7\alpha + 4\beta + ^{207}\text{Pb} + \nu_e$) is 46 MeV, with 2.1 MeV neutrino energy (Stacey and Davis, 2008). The neutrino energy carried off is subtracted so we have a gravitational transformity for ^{235}U as follows:

$$g\tau_{235U} = (2.06E - 11 \text{ gej}) / (43.9 \text{ MeV}) = 2.93 \text{ gej} / J_{235U}$$

The ^{238}U reaction,



yields an energy/atom of ^{238}U equal to:

$$9.73E - 13 \text{ gej} + 33(3.6E - 15 \text{ gej}) + (33 + 50)[2(1.22E - 13 \text{ gej})] = 2.14E - 11 \text{ gej}$$

The energy released during complete decay of ^{238}U ($^{238}\text{U} \rightarrow 8\alpha + 6\beta + ^{206}\text{Pb} + \nu_e$) is 52 MeV, with 4.3 MeV neutrino energy (Stacey and Davis, 2008). The neutrino energy carried off is subtracted leaving a gravitational transformity for ^{238}U as follows:

$$g\tau_{238U} = (2.13E - 11 \text{ gej}) / (47.7 \text{ MeV}) = 2.80 \text{ gej} / J_{238U}$$

Solar Equivalence Ratios of Radionuclides

An SER for radionuclides [units=seJ/J]⁵ can be computed using the gravitational transformity for Sunlight, and gravitational transformities for radionuclides and assuming an equivalence between the two ratios formed by the gravitational transformities (Eq. ((2-3)).

$$SER = \frac{\frac{gej}{J_{radionuclide}}}{\frac{gej}{J_{Solar}}} = \frac{g\tau_R}{g\tau_S} = \frac{seJ}{J_{radionuclide}} \quad (2-3)$$

$$SER_{40K} = (6.16 \text{ gej} / J_{40K}) / (7.65E - 4 \text{ gej} / J_{Sunlight}) = 8,050 \text{ seJ} / J$$

$$SER_{232Th} = (3.18 \text{ gej} / J_{232Th}) / (7.65E - 4 \text{ gej} / J_{Sunlight}) = 4,160 \text{ seJ} / J$$

⁵ since SER is in solar equivalent joules, we capitalize the J in the term seJ (see Brown and Ulgiati, 2016)

$$SER_{235U} = (2.93 \text{ geJ}/J_{235U}) / (7.65E - 4 \text{ geJ}/J_{Sunlight}) = 3,840 \text{ seJ}/J$$

$$SER_{238U} = (2.80 \text{ geJ}/J_{238U}) / (7.65E - 4 \text{ geJ}/J_{Sunlight}) = 3,660 \text{ seJ}/J$$

Table 2-5 summarizes the solar equivalence ratios for the radionuclides.

Summary

It's well known that sunlight and radionuclides are generated when gravitational exergy converts matter into energy. The cumulative gravitational exergy required in certain fusion reaction cycles is used to underscore the gravitational energy of both sunlight and radionuclides. We define a gravitational transformity for sunlight and radionuclides ($g\tau_S$ and $g\tau_R$) respectively as the ratio of gravitational energy to either sunlight or radionuclide exergy.

Next we introduced a solar equivalence ratios (SER) which expresses radiogenic energy in solar equivalent energy. These results are a major contribution in two respects. First, up until now there was no energy characterization (transformity or otherwise) for radioisotopes. Hence there was no ability before now to assess the energy of nuclear fuels or of the nuclear heat that contributes the geothermal exergy. Second, this work eliminates the inconsistent terminology of referring to the GEB (geobiosphere energy baseline) as solar energy, which it is not. If it is any form of energy the GEB is gravitational energy. When expressed in solar equivalent energy the GEB can be agglomerated into a single unit, the seJ, which is not energy, but rather a solar equivalence.

These results can principally be applied to the recalculation of the GEB, i.e. the newly discovered energy of radionuclides. Also the method of computing gravitational exergy will be used in Chapter 3 for the other main biosphere sources, primordial heat

and Earth's rotational kinetic energy. Finally, as in Chapter 4, the nuclear energy of Uranium will be accounted in the total energy accounting of the US economy.

EndNote 1: This may seem odd at first, until we recognize two important factors that cause this UEV to be smaller than we would intuitively expect. The first is that nuclear fusion is a quantum mechanical process that involves a phenomenon called quantum tunneling, whereby a proton can sometimes tunnel over the coulomb barrier into another atom even if it does not have sufficient energy to overcome the coulomb repulsion force according to classical electrodynamics. In fact, we can calculate the energy per reaction required to overcome the coulomb barrier for proton-proton fusion as the Coulomb potential:

$$U = \frac{e^2}{4\pi r \epsilon_0} = \frac{(9 * 10^9 Nm^2/c^2)(1.60 * 10^{-19}C)^2}{3 * 10^{-15}m} = 7.68 * 10^{-14}J$$

This is two orders of magnitude greater than our average energies of 6.5×10^{-16} J/reaction and in fact corresponds to temperatures of $(2/3)(7.68 \times 10^{-14})/(2k_B) = 1.9 \times 10^9$ K, which the Sun does not reach. The reason that fusion reactions occur in significant quantities in the Sun is that the core contains so many protons that the probability of fusion occurring is very high.

The second reason for such a low UEV is that, although very little mass is lost in the fusion reactions, and the total number of protons is always conserved, the small amount of mass that is transmuted during each reaction has relatively large energies according to the energy-mass equivalence $E=mc^2$. The energy of this mass lost is not included because it has different units than the gravitational exergy used in the fusion reaction. We would need to assume some gravitational energy responsible for the initial cosmic production of protons, which is yet beyond our clear understanding.

EndNote 2: The heavy radionuclides (^{238}U , ^{235}U , and ^{232}Th) are all products of r-process nucleosynthesis, whereby seed nuclei under extreme conditions of high

temperatures and high neutron flux rapidly capture neutrons to form the heaviest elements (Burbidge et al., 1957; Cameron, 1957). Core-collapse supernova are widely considered to be the main progenator of r-process nucleosynthesis, but the exact site of the supernova at which this takes place is debated (Matthews and Cowan, 1990; Cowan et al., 1991; Takahashi et al., 1994). Currently, the primary opinion is that the ideal conditions are most likely met in a “hot bubble” region of high density neutrino flux at the surface of a newly formed protoneutron star (Meyers et al., 1992; Woosley et al., 1994; Surman et al., 2013).

All stars greater than 8 solar masses undergo gravitational collapse of the eventual iron core, resulting in type II supernova explosions. (Weaver and Woosley, 1993). In these core-collapse supernova the iron peak nuclei disintegrate into alpha particles, then protons and neutrons. The collapsing electron pressure from the previously degenerate state converts protons to neutrons and emits neutrinos ($p^+ + e^- \rightarrow n + \nu_e$) and a neutron core that itself becomes degenerate. The protoneutron star at nuclear density rebounds the energy of gravitational collapse. The shock wave perpetuated outward has energies on the order of 2×10^{53} erg (Thielemann et al., 1998). However, 99% of this energy is carried by neutrinos, leaving only 1% as shock-wave-generated thermal energy. This thermal energy takes the form of a rapidly expanding, high-energy, high-entropy bubble, which is likely the site of r-process synthesis of heavy nucleides. Temperatures here are related to the rebounded shock energy ($E_0 = 0.01(2 \times 10^{53} \text{ erg}) = 2 \times 10^{51} \text{ erg}$) by the radiation energy density equation, $E_0 = VaT^4$ where V is the volume ($4\pi r^3/3$), and a is the radiation density constant $7.564 \times 10^{-15} \text{ erg cm}^{-3} \text{ K}^{-4}$.

For a radius of 3700 km, corresponding to r-process radius of a 20 solar mass star (Pagel, 2009), this shock energy translates to average r-process temperatures of 5.9×10^9 K, and energies of $1.22\text{E-}13$ J/particle.

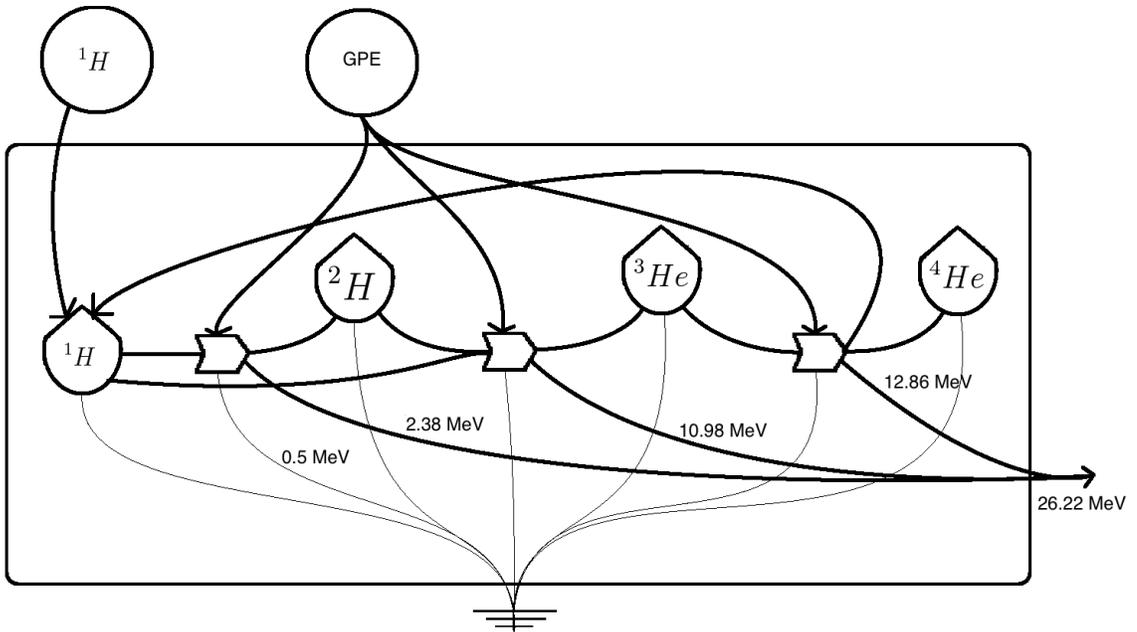


Figure 2-1. PPI chain of reactions showing inputs of hydrogen and gravitational potential exergy (GPE) and the output of 26.202 MeV of solar exergy. Note a total of 0.53 MeV of exergy are carried away as neutrino decay (Huang and Yu, 1998; Figure from Siegel et al. 2016).

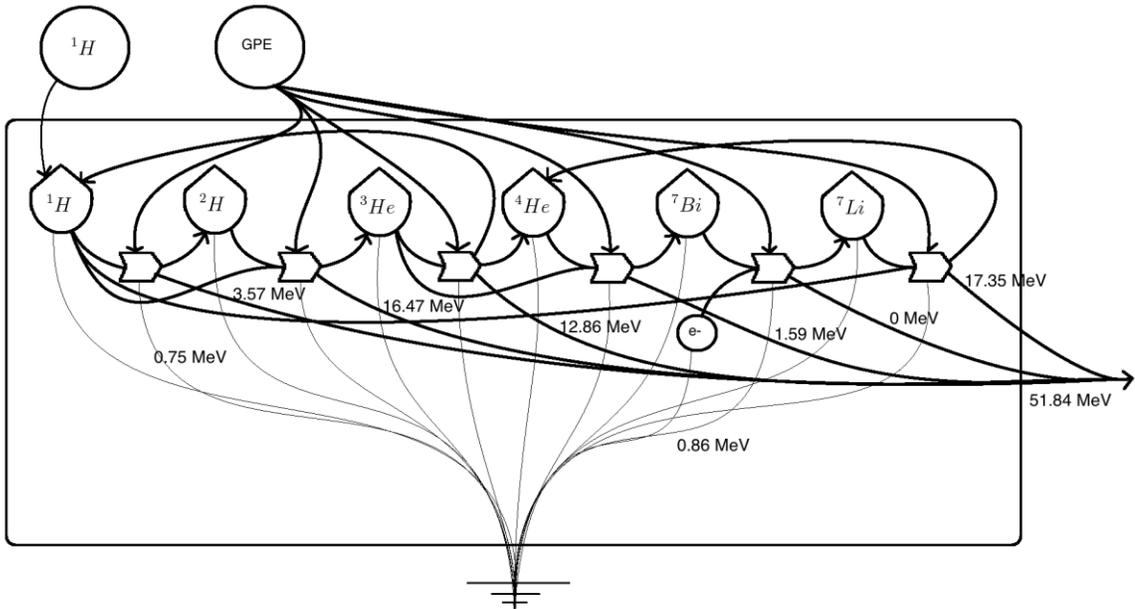


Figure 2-2. PPII chain of reactions showing inputs of hydrogen and gravitational potential exergy (GPE) and the output of 51.807 MeV of solar exergy. Note a total of 0.795 MeV of exergy are carried away as neutrino decay. (Huang and Yu, 1998; Figure from Siegel et al. 2016).

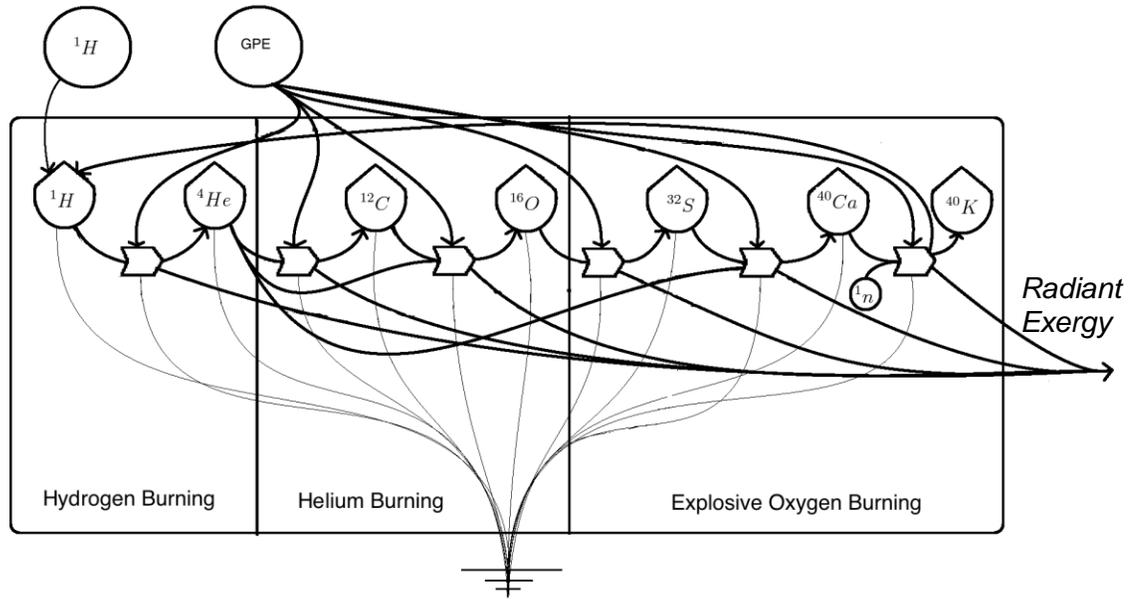


Figure 2-3. ^{40}K nucleosynthesis showing inputs of gravitational potential exergy (GPE) and hydrogen required during helium burning followed by explosive oxygen burning (Figure from Siegel et al. 2016).

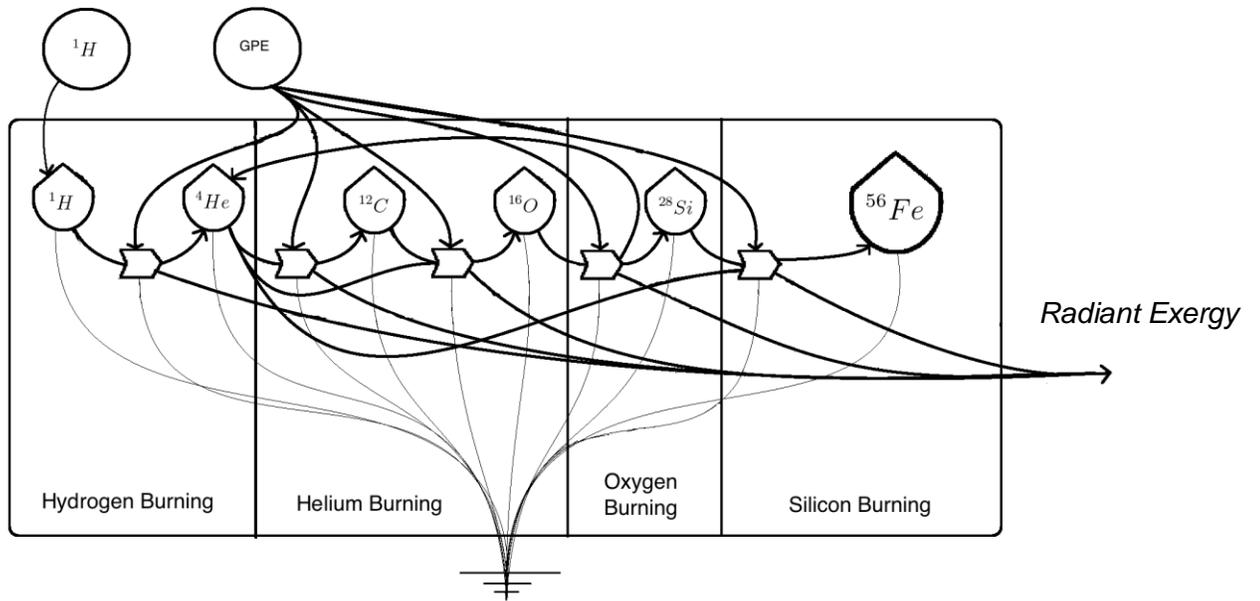


Figure 2-4. Non-explosive nucleosynthesis of ^{56}Ni showing the input of gravitational potential exergy (GPE) and the input of hydrogen for the first reaction that produces helium, followed by the required reactions during helium, oxygen and silicon burning (Figure from Siegel et al. 2016).

Table 2-1. Gravitational energy accounting for the p-p 1 cycle

Reaction	T (Kelvin)	Total thermal geJ ^a	Solar output (MeV) ^b	geJ/Solar J	Reactions/final product
${}^1\text{H}(p, e^+\nu)^2\text{H}$	1.57E+07	6.50E-16	1.442 ^c		2
${}^2\text{H}(p, \gamma)^3\text{He}$	1.57E+07	6.50E-16	5.494		2
${}^3\text{He}({}^3\text{He}, 2p){}^4\text{He}$	1.57E+07	6.50E-16	12.860		1
Total		3.25E-15	26.202 ^d	0.000775 ^e	

a. Gravitational potential exergy required is computed using Eq 2-1 and the Sun's temperature of 15.7E6 K, yielding 3.25 E-16 J/particle, 2 particles per reaction.

b. Radiation output from Huang and Yu (1998).

c. Approximately 0.265 MeV neutrino (ν_e) energy is carried away during the first reaction in the PPI chain (Huang and Yu, 1998). Neutrinos do not contribute to Sunlight, so they are not part of our radiation output and are subtracted

here. There are two first reactions per final product, so 0.53 MeV is subtracted from final solar output.

d. The total is the sum of solar output per reaction multiplied by reactions per final product.

e. Gravitational transformity is total thermal gravitational energy (geJ) divided by total solar output converted to joules (1.60 E-13 J/MeV).

Table 2-2. Gravitational energy accounting for the PPII cycle

Reaction	T (Kelvin)	Total thermal geJ ^a	Solar output (MeV) ^b	geJ/Solar J	Reactions/final product
${}^1\text{H}(p, \beta^+\nu)^2\text{H}$	1.57E+07	6.50E-16	1.442		3
${}^2\text{H}(p, \gamma)^3\text{He}$	1.57E+07	6.50E-16	5.494		3
${}^3\text{He}({}^3\text{He}, 2p){}^4\text{He}$	1.57E+07	6.50E-16	12.860		1
${}^3\text{He}({}^4\text{He}, \gamma){}^7\text{Be}$	1.57E+07	6.50E-16	1.588		1
${}^7\text{Be}(e^-, \nu){}^7\text{Li}$	1.57E+07	~	0.862		1
${}^7\text{Li}(p, {}^4\text{He}){}^4\text{He}$	1.57E+07	6.50E-16	17.346		1
Total		5.85E-15	51.807 ^c	0.000705 ^d	

a. Gravitational Potential Exergy required is computed using Eq 1 and Sun's temperature of 15.7×10^6 K, yielding 3.25 E-16 J/particle.

b. Radiation output from Huang and Yu (1998).

c. The total is the sum of solar output per reaction multiplied by reactions per final product.

d. Gravitational transformity is total thermal gravitational energy (geJ) divided by total solar output converted to joules (1.60 E-13 J/MeV).

e. 0.265 MeV is the approximate neutrino (ν_e) energy carried away during the first reaction of the PPII Huang and Yu (1998). Neutrinos do not contribute to Sunlight, so they are not part of our radiation output and is therefore is not included. There are 3 first reactions per final product in the PPII cycle. Also 0.862 MeV neutrino energy is released during the fusion of beryllium with an electron to form lithium. This too is subtracted from the final solar output.

Table 2-3. Gravitational energy accounting for the nucleosynthesis of ^{40}K .

Input	T (Kelvin)	Total thermal geJ	Reactions/final product
$^4\text{He}(\alpha)^8\text{Be}$	3.00E+08	1.24E-14	2
$^8\text{Be}(\alpha, 2\gamma)^{12}\text{C}$	3.00E+08	1.24E-14	2
$^{12}\text{C}(\alpha, \gamma)^{16}\text{O}$	3.00E+08	1.24E-14	2
$^{16}\text{O}(^{16}\text{O})^{32}\text{S}$	3.50E+09	1.45E-13	1
$^{32}\text{S}(\alpha, \gamma)^{36}\text{Ar}$	3.50E+09	1.45E-13	1
$^{36}\text{Ar}(\alpha, \gamma)^{40}\text{Ca}$	3.50E+09	1.45E-13	1
$^{40}\text{Ca}(n, p)^{40}\text{K}$	3.50E+09	1.45E-13	1
Total less ^4He		6.54E-13 ^a	
Total with 10 used ^4He		6.91E-13 ^b	

a. Total thermal geJ multiplied by reactions per final product, summed.

b. Total less 4He plus the total thermal geJ of ^4He synthesis (averaged from PPI and PPII cycles) that is used in this reaction chain. A total of 10 Helium atoms were used to create ^{40}K , each possessing 3.62 E-15 geJ.

Table 2-4. Gravitational energy accounting of non-explosive nucleosynthesis of ^{56}Ni .

Input	T (Kelvin) ^a	Total thermal geJ	Reactions/final product
$^4\text{He}(\alpha)^8\text{Be}$	3.00E+08	1.24E-14	2
$^8\text{Be}(\alpha, 2\gamma)^{12}\text{C}$	3.00E+08	1.24E-14	2
$^{12}\text{C}(\alpha, \gamma)^{16}\text{O}$	3.00E+08	1.24E-14	2
$^{16}\text{O}(^{16}\text{O}, \alpha)^{28}\text{Si}$	1.50E+09	6.21E-14	1
$^{28}\text{Si}(\alpha, \gamma)^{32}\text{S}$	2.70E+09	1.12E-13	1
$^{32}\text{S}(\alpha, \gamma)^{36}\text{Ar}$	2.70E+09	1.12E-13	1
$^{36}\text{Ar}(\alpha, \gamma)^{40}\text{Ca}$	2.70E+09	1.12E-13	1
$^{40}\text{Ca}(\alpha, \gamma)^{44}\text{Ti}$	2.70E+09	1.12E-13	1
$^{44}\text{Ti}(\alpha, \gamma)^{48}\text{Cr}$	2.70E+09	1.12E-13	1
$^{48}\text{Cr}(\alpha, \gamma)^{52}\text{Fe}$	2.70E+09	1.12E-13	1
$^{52}\text{Fe}(\alpha, \gamma)^{56}\text{Ni}$	2.70E+09	1.12E-13	1
Total less ^4He		9.20E-13 ^b	
Total with 14 used ^4He		9.70E-13 ^c	

a. The temperatures at which these hydrostatic burning stages operate and their required gravitational exergy are from (from Woosley et al., 2002).

b. Total thermal geJ multiplied by reactions per final product, summed for the column.

c. Total less ^4He plus total thermal geJ of the synthesis of the 14 ^4He used to create ^{56}Ni (averaged from PPI and PPII cycles). Each ^4He possesses 3.62 E-15 geJ.

Table 2-5. Solar Equivalence Ratios (SER) for Radionuclides

Isotope	Gravitational transformity (gej/J)	SER ^{a.} (seJ/J)
⁴⁰ K	6.16	8.05E3
²³² Th	3.18	4.16E3
²³⁵ U	2.93	3.84E3
²³⁸ U	2.80	3.66E3

a. Computed by dividing isotope gravitational transformity by the gravitational transformity of solar exergy (7.65 E-4 geJ/J).

CHAPTER 3 COMPUTING THE GEOBIOSPHERE EMERGY BASELINE: A NOVEL APPROACH

Research Impetus

In Chapter 3 we expand the approach from Chapter 2 to compute solar equivalent energy for the Earth's tidal dissipation and deep heat. The motivation for this new approach came from a sequence of realizations and questions regarding the previous method which accounts the GEB (geobiosphere emergy baseline).

- It's inappropriate to label the ratio of solar exergy¹ to tidal exergy, or of solar exergy to geothermal exergy, a *transformity*. This ratio of seJ J^{-1} tidal or geothermal exergy is a 'solar equivalence ratio', rather than 'solar transformation ratio' (Raugei, 2013).
- There were no nuclear UEVs (e.g. $\text{seJ J}^{-1} {}^{238}\text{U}$)².
- Recognition that the Earth's primordial heat and radiogenic heat are derived from two different processes and potentially have different transformities.
- Recognition that the interaction of gravitational potential of the Earth-Moon-Sun system with Earth's rotational kinetic energy is responsible for the tides. Specifically, Earth's rotation kinetic energy is dissipated directly via tidal friction.
- Finally, we postulated that it might be possible to express sunlight, Earth's rotational kinetic energy, radiogenic heat and Earth relic heat in a single quantity, the gravitational potential energy dissipated to produce them.

The new approach in this paper evaluates the gravitational exergy dissipated in to produce geothermal and tidal exergy. From this, gravitational transformities are found for each exergy source. From these gravitational transformities we can make equivalences between all the sources. The GEB is commonly expressed in solar equivalents and so solar equivalent energy is the obvious unit of choice our GEB.

¹ Exergy, as defined in Chapter 2, is available potential energy of a particular form. Hence solar exergy is equivalent to the phrase solar available potential energy.

² This chapter's rational impetus chronologically came before the previous chapter and set the logical foundation for using GPE as the common progenitor of radionuclides and other Earth energy sources.

A basic paradigm being challenged with our approach is that of backwards calculated equivalences (Raugei, 2013). Since solar energy does not actually contribute to radiogenic heat, Earth's relic heat or its rotational kinetic energy, it is apparent that these latter sources do not embody solar exergy and are inappropriately characterized by solar energy. As is well understood, in the past, computation of Earth's deep heat and tidal energy input involved backwards calculation of equivalents to express each of these sources as solar equivalent energy (Odum, 2000a). In this new approach we utilize forward calculation of the gravitational potential energy (GPE) that was dissipated to produce Earth's exergy sources.

GPE, or gravitational exergy, can be shown to be the progenitor of sunlight, radioisotopes, Earth's primordial heat (heat left from the gravitationally induced accretion process), and tidal energy (interaction of Earth-Moon-Sun gravitation with Earth's rotational KE). The objective of our forward computation approach is to calculate gravitational transformities (gej/J) for the geobiosphere's sources. From these ratios ($gej J^{-1}$), solar equivalent energy ratios ($seJ J^{-1}$)³ using the ratio of gej/J of sunlight can be computed to express each source in a common unit. Once expressed as a common unit (seJ) the sources may be added to express the sum of Earth's driving exergy sources, the GEB. Table 3-1 shows the relationships between gravitational transformities and solar equivalent energy of each Earth exergy source.

³ Solar equivalent Joule (seJ) differs from solar emjoule (sej). The units of solar equivalent energy are solar equivalent Joules, abbreviated seJ (note the capital J). The abbreviation of the energy unit, Joule, is always capitalized, thus solar equivalent Joules are abbreviated using a capital J. A lower case 'j' in sej represents solar-emergy-joule, or solar emjoules. An emjoule is not available energy, it is the memory of available energy destroyed in the past, and thus we use the lower case "j". The GEB is expressed in $seJs$ (solar equivalent Joules) whereas subsequent geobiospheric resources (e.g. wind, rain, fossil fuels, etc.) are expressed in sej (solar emjoules). The distinction is not arbitrary as it clarifies that the independent energies driving the geo-biosphere (i.e. geothermal energy, Earth's tidal energy, and radionuclides) are in no way directly or indirectly a transformation of Sunlight. Therefore, they do not embody solar energy and are thus more appropriately characterized by equivalences than transformities.

Methods

We posit that gravitational exergy (GPE) is the driver of higher quality energies like concentrated heat, sunlight, fused matter, and rotational energy. For our purposes GPE is the lowest quality energy from which the others can be computed. Odum (in Brown et al., 2004) wrote:

In the vast realm of space, stars and other units that self-organize are gravity produced... Under the pull of gravity, units of matter condense, storing energy and developing structure. The resulting increased gravity captures more material. The potential energy of mass falling inward together is concentrated and transformed into heat and energy of rotation. When the gravity and temperature are high enough, fusion reactions convert the mass of hydrogen into energy, turning such units into light-emitting stars.

The following paragraphs outline the methods and assumptions necessary for to compute solar equivalences for each Earth exergy source.

Redefinition of Geothermal and Tidal Inputs

Deep Heat

To accurately account Earth's deep heat, Earth's primordial heat and radiogenic heat should be accounted separately. Deep heat was the term used in the past for the combined geothermal inputs to the geobiosphere that came from the internal energy of the Earth and heat from radiogenic sources. These are independent sources of heat energy, which are generated from different processes and therefore should have different UEV formulations. Thus we have separated geothermal inputs to the geobiosphere into primordial heat and radiogenic heat and computed separate UEVs for each.

Tidal Energy

Gravitational attraction of the Earth/Moon/Sun system interacts with Earth's rotational KE to produce tides on Earth. Over the years the energy community has referred to the input of energy to the geobiosphere from this phenomena as tidal input, tidal potential, tidal momentum, or tidal energy. The energy input is relatively well known at about $1.17 \text{ E}20 \text{ J y}^{-1}$ (Munk and Wunsch, 1998). Most of this energy dissipates in the oceans (about 96%) while a small fraction is dissipated in the land masses (4%) and minute amounts in the atmosphere (e.g. Coriolis winds).

The astrophysical result of the gravitational “pull” by the Moon (and to a lesser extent by the Sun) is that kinetic energy of the Earth’s rotation is dissipated. It is partly transformed into thermal energy and partly contributes to the increasing orbital potential energy of the Moon. Earth’s rotation is slowing and the moon is moving farther away. The relationship between Earth's decreasing rotational KE and tidal exergy is direct. Thus a solar equivalent energy ratio for Earth’s rotational KE is used to approximate the solar equivalent energy of tides.

Gravity Produces Sunlight

To summarize the finding of Chapter 2, essentially, thermal temperatures were used to calculate translational kinetic energy of particles that fuse in the Sun. Assuming kinetic energy is equal to GPE, only the reference frame changes (according to Einstein), this translational kinetic energy became the numerator in the ratio of gravitational transformity for sunlight. The denominator is the quantity of sunlight output from the fusion reactions responsible for our Sun's light.

In large part, the Sun's light is produced from what are known as the PPI and PPII fusion cycles (Table 3-2). The weighted average of the gravitational transformities

of these two cycles compose the gravitational transformity of Sunlight ($7.65 \text{ E-04 geJ J}^{-1}$). That is, 1,320 J Sunlight are yielded for every joule of gravitational energy supplied (see Chapter 2 Endnote 2).

Gravity Produced the Heavy Elements

The production of heavy isotopes is fundamentally similar to the production of sunlight. However, it requires much hotter temperatures, thus heavier elements require more gravitational energy than lighter elements. Heavier than iron elements are only produced in stars far more massive than our Sun. In fact, the extreme temperatures in combination with the necessary chemical constituents required for synthesis of elements heavier than iron may only occur in the end of life type II supernova of a massive star.

A summary of the gravitational transformities of Earth's major radioisotopes is given in Table 3-3. The transformity of the elements decreases with weight, in what seems to be a contradiction to the statement above about heavier elements requiring more energy to synthesize them. However, the decreasing transformities are the result of the heavier elements having higher decay energies (the denominator in the ratio of geJ J^{-1}).

Gravity Produced Earth's Rotational Energy and Primordial Heat

Production of the Earth's rotational energy and primordial heat are coupled. GPE dissipated during the formation of the Earth produced both relic heat and the Earth's rotational energy (Figure 3-1).

Earth's Rotational Energy

Earth's gravitational binding energy represents the GPE required to produce a "solid Earth" out of the protoplanetary disk of gas and dust. Gravitational binding energy

of a system is the energy required to “unbind” the system by overcoming gravity and separating the system into a diffuse mass infinitely far away from its center of mass. Back-calculating Earth's binding energy is equal to the work done by gravity to bring the matter together from infinite distance. Consider Earth a spherical mass of uniform density, the gravitational binding energy G_E is a function of the gravitational constant, $G = 6.674 E - 11 Nm^2kg^{-2}$, and Earth’s mass, $M = 5.97 E24 kg$ and radius, $R = 6.37 E6 m$ (Eq. ((3-1)).

$$G_E = \frac{3GM^2}{5R} = 2.24 E32 J \quad (3-1)$$

However, given that Earth has a non-uniform density profile, the actual binding energy computed by Stacey and Davis (2008) is $G_E = 2.49 E32 J$. From this, Earth’s original rotational kinetic energy $K_{E,0}$ and thermal energy $Q_{E,0}$ were formed.

Earth's rotational KE is the transformation of primordial GPE which accreted the Earth (dePater and Lissauer, 2010). Some rotational energy may have come from frictional drag with the protoplanetary disk, however most was accumulated from the relative motions of accreted material. Earth's rotational KE gradually transforms into lunar geopotential energy and some of it dissipates as heat. The rotational energy is not replenished on any time scale, it only dissipates. Earth's rotation kinetic energy is expressed in Eq. (3-2).

$$K_E = \frac{I\omega^2}{2} = 2.13 E29 J \quad (3-2)$$

Where I and ω are respectively Earth's moment of inertia ($\sim 8.01 E37 kgm^2$; Wolfram Alpha, 2015) and angular velocity ($\sim 7.29E-5 rad/s$; Wolfram Alpha, 2015). The angular momentum of the Earth-Moon system is conserved. Even as the rotation of Earth slows and its rotational KE is translated to heat and lunar orbital potential energy,

angular momentum of the system is conserved. The Earth-Moon angular momentum L (Morishima and Watanabe, 2004) is the product of its moment of inertia and angular velocity Eq. (3-3).

$$L = I\omega = 3.46 E34 Js \quad (3-3)$$

This momentum was once contained solely in the Earth, assuming the moon was formed via a giant impact with a mars sized object (Canup, 2014). Holding L constant (conservation of angular momentum) we can find ω_0 of the Earth by substituting Earth's original moment of inertia, $I_{E,0}$. Moment of inertia is linearly related to mass of the object, assuming uniform density. For an estimate we can approximate $I_{E,0} = I_E \left(\frac{m_E + m_m}{m_E} \right) = 8.10 E37 kgm^2$; where $\left(\frac{m_E + m_m}{m_E} \right)$ is the percent increase of the Earth's mass when added with the Moon's mass (7.35 E22 kg). The original angular velocity of the Earth was approximately $\omega_0 = L/I_{E,0} = 4.27 E - 4 rad/s$ (or a rotation of about 4.09 hr/day). At this speed, using Eq (3-2), $K_{E,0} = 7.29 E30 J$.

Earth's Primordial Heat

The original thermal energy $Q_{0,E}$ of the Earth is the current thermal energy Q plus the heat flux since the origin of Earth $\frac{dQ}{dt}$ (Eq. (3-4)). Labrosse and Jaupart (2007) show that the annual $\frac{dQ}{dt} \cong 35 TW$ since circa 4.5 Ga for a total of about 5.0E30 J. The current internal thermal energy is $Q = 1.7 E31 J$ (Jaupart et al., 2007).

$$Q_{E,0} = \frac{dQ}{dt}t + Q = 2.20 E31 J \quad (3-4)$$

A summary of the flows of energy in the formation of the Earth is given in Table 3-4 and summarized in Figure 3-1.

Results

Radiogenic Heat Contributions

We estimate that the percent of relative radiogenic heat flux from ^{238}U , ^{232}Th and ^{40}K is 40%, 40% and 20% respectively. These are rounded estimates from recent KamLAND neutrino detection experiments for ^{238}U and ^{232}Th energy contributions (Gando et al., 2011) and the bulk silicate Earth (BSE) predicted value for ^{40}K (McDonough and Sun, 1995). We use an average geothermal contribution from radiogenic sources of 15.7 TW, which is 45% of total geothermal input of 34.6 TW (Brown and Ulgiati, 2016). The exergy contribution of radiogenic heat to the geobiosphere from each of the radioisotopes is given in column 3 of Table 3-5, and the total energy contribution to the GEB is in the last column.

Split of the GPE to Generate Earth Rotational KE and Primordial Heat

How to allocate GPE to the coupled products of accretion, Earth's rotational KE and primordial heat, is complicated. We recognize five options for assigning GPE to Earth rotational KE and primordial heat (Table 3-9). First was to assign the GPE to each of the products based on an efficiency of production on each pathway, however these efficiencies are unknown.

Two of the other options are by-product allocations, which assign GPE to either one of the two products equal to their energy, and assign the remainder (the dissipated portion) to the other. That is, one product is assumed equal in quality to the driving gravitational exergy, and the other product is considered the "primary" product and is characterized by a higher transformity commensurate with its quality upgrade. These two options represent the two extremes in the range of possibilities and bounds the possible UEVs for rotational KE and relic heat between maximum and minimum (1

gej/J) gravitational transformities. This by-product method is undesirable because neither the deep heat or tides are equivalent in quality to the gravitational exergy which created them as evidenced by the concentration of Earth's relic heat and rotational KE relative to its background solar system from which it was formed.

A fourth option was to treat the accretion process as a split of the GPE. A split avoids the drawback of characterizing either rotational KE or relic heat as equal in quality to the gravitational exergy which produced it. However, a split makes rotational KE and relic heat equal in quality to each other, which while not yet provably false, is highly unlikely.

A final option is a co-product procedure. If we consider rotational KE and relic heat co-products we must perform emergy algebra when computing the GEB. That is the smaller of the two, KE and relic heat, would not be added to the GEB that resulted (fourth rule of emergy algebra; Brown and Herendeen, 1996). The drawback here is that the GEB becomes more cumbersome, especially when evaluating regions of the Earth where both tides and deep earth heat are accounted, and also because the co-product method inflates the resultant GEB as shown by its final numerical result, which is noticeably bigger than the other options presented above.

We chose the split method (option 4) where the input GPE is split into the products proportionally based on the original quantity of energy stored from each product. This results in equal UEVs for Earth rotational KE and primordial heat. While we feel that this is imperfect, the GEB that results from this allocation procedure is very similar to both by-product methods (options 2 and 3 above) and similar to the co-product allocation (option 5 above).

Note that the final value suggested by this paper only indirectly effects the GEB number used in future emergy evaluations. Two other publications on this topic were contemporaneously forged alongside this one, both of which utilize the backwards calculation paradigm, and the results of this study here bolsters the results from those other two studies (Brown et al., 2016). Although the backwards calculation is less theoretically desirable, it is stronger in the sense that the data used in that approach is much more reproducible. The data used for this publication, in particular the primordial relic heat and the GPE used to form the Earth, are highly uncertain. This Chapter serves other purposes, which are explicated in the conclusions, then to offer a precise number for the GEB. However, the similarity of our forwards calculated results with those of the backwards calculated publications is a promising discovery and strong asset in the case to be made for utilizing a concept such as the GEB in environmental accounting.

Earth Rotational KE and Primordial Heat UEVs

The transformation of primordial GPE into Earth's rotational KE and internal thermal energy are considered a split. Splits by definition give equal UEVs for both products. Realistically, rotational energy and relic heat accomplish different kinds of work, an indication of different transformities. However, see the previous section.

SERs (solar equivalence ratios) for rotational KE and primordial thermal exergy are given in Table 3-6. In this method of computation, we first proportionally allocate the GPE between the two pathways (Figure 3-1) and then compute a gravitational transformity (gej J^{-1}) for each. The gravitational transformity of each was divided by the gravitational UEV of sunlight ($\text{gej J}_{\text{solar}}^{-1}$). The resulting SER for both is 11,100 seJ J^{-1} .

Earth Tidal Input

Tidal input energy input to the geobiosphere is known to be about $1.17 \text{ E}20 \text{ J y}^{-1}$ (Munk and Wunsch, 1998). We assume the loss of Earth rotational KE is equal to the tidal drag that results from the combined Earth/Moon/Sun system. Thus the global energy of tides are the product of the tidal exergy ($1.17 \text{ E}20 \text{ J y}^{-1}$) and the UEV of Earth's rotational KE given in Table 3-6 ($11,100 \text{ seJ J}^{-1}$) which is $1.30 \text{ E}24 \text{ seJ y}^{-1}$. This is the contribution from Earth's rotational KE to the GEB.

Primordial Heat Contributions

We estimate a primordial heat contribution of 18.9 TW, which is 55% of total geothermal exergy input of 34.6 TW (Brown and Ulgiati, 2016). Total primordial thermal exergy is $5.95 \text{ E}20 \text{ J y}^{-1}$ after applying Carnot ratios to deep heat (Ibid.). The product of accretion heat exergy with its UEV from Table 3-6 ($11,100 \text{ seJ J}^{-1}$) results in the empower contribution of $6.62 \text{ E}24 \text{ seJ y}^{-1}$ from relic heat.

The Geobiosphere Energy Baseline

Table 3-7 lists the main sources of exergy to the geobiosphere of Earth. The first column lists footnotes for each entry. The second column lists each item. The third column is the exergy flux of each input. The fourth column is the SER and the fifth column is the solar equivalent flux (seJ/yr) to the geobiosphere computed as the product of the third and fourth columns. The UEVs for primordial heat and the Earth rotational KE (tidal dissipation) are a split based on our assumption above. The GEB is the sum of the last column. Computed in this manner the GEB totals $13.9 \text{ E}24 \text{ seJ y}^{-1}$.

Average Solar Equivalences

Table 3-8 lists the SERs for the three main sources of renewable inputs to Earth's geobiosphere, where the SER of the geothermal input is a weighted average of

primordial and radiogenic SERs in proportion to their annual exergy flux. The two sources of geothermal exergy have distinct SERs however heat flow databases (e.g. International Heat Flow Database) provide data that is not differentiated between primordial and radiogenic sources. They combine the sources into one "heat flow". It seems appropriate to provide a general "heat flow" SER as the weighted average SER for both geothermal inputs. The estimated percent of total heat from primordial and radiogenic sources is 55% and 45% respectively. A weighted average of these two sources yields the SER for geothermal exergy of $8,200 \text{ seJ J}^{-1}$. For processes that specifically utilize nuclear exergy, the radionuclide SERs should be used.

Summarized Findings

Our method here is a "forward computation" of solar equivalences using the gravitational potential energy required to produce the main sources driving Earth's geobiosphere. First, the forward computation method for the GEB presented here is one of a kind and it closely approximates the results the other widely recognized backwards calculated methods. The similar results between other backwards computations and our forward computation at least somewhat validates our model and its assumptions and fortifies the numerical quantity we use to express the GEB. The best solution found here is the one which considers accretion heat and rotational kinetic energy of the Earth as splits. This is because in the split method we acknowledge both relic heat and rotational KE have gravitational transformities greater than unison, which is fact. It is also not farfetched because of the fact that a small portion of tidal dissipation occurs in the solid earth, known as earth tides. This kind of tide is directly transformed into deep earth heat, and so would actually have essentially an identical energy characterization.

Even though co-product method applied to the GEB recognizes unique and greater than unison SERs in Earth's accretion products, co-product method applied here is cumbersome and inflates the GEB. Using the split assumption Earth's GEB is $13.9 \times 10^{24} \text{ seJ y}^{-1}$.

We recognize two sources of geothermal exergy to the geobiosphere, radiogenic and primordial. These sources have different gravitational transformities reflecting their different origins. We used the SERs for radioisotopes from Chapter 2 to find the contribution of radiogenic heat to the geobiosphere. We also computed SERs for primordial heat and Earth's rotational KE. We used the emergy of Earth's rotational KE as a way to estimate the emergy of Earth's tides. Most of the gravitational interaction between the Earth/Moon/Sun system, which is expressed as a decrease in rotational KE of Earth, is converted to heat by frictional losses in the oceans (see notes in Table 3-9). Thus an SER for Earth's rotational KE closely represents the SER of tidal dissipation.

Understand that our proposed method of computing the SERs of global exergy sources uses very different time/space boundaries compared with all previous and current methods. The assumptions made in the forward computation method are particularly vexing and obviously include large uncertainties. This exercise in computing the GEB was initiated as one of several approaches and it will not drive the ultimate decision on a unified GEB but will provide valuable input. Combined with the results of other methods our analysis strengthens the final unified GEB by virtue of the fact that it approaches the computation from a forward computational method, a method in striking contrast to the others, yet yields a very similar result.

Table 3-1. Summary of proposed relationship between solar Joules and the remaining exergy sources to the geobiosphere

Geobiosphere energy source	Transformity symbol	Units	Solar equivalent Joules / Joule (seJ J ⁻¹)
Sunlight	$\varphi\tau_s$	gej/J	1
Radiogenic heat	$\varphi\tau_S$	gej/J	$\varphi\tau_R/\tau_S$
Primordial heat	$\varphi\tau_Q$	gej/J	$\varphi\tau_Q/\tau_S$
Tidal energy	$\varphi\tau_K$	gej/J	$\varphi\tau_K/\tau_S$

Table 3-2. Summary of gravitational transformities for Sunlight (from Siegel et al., 2016).

	PPI cycle	PPII cycle	Weighted average
Gravitational transformity (gej/J)	7.74 E-4	7.10 E-4	7.65 E-4
Contribution to total solar output	86%	14%	

Table 3-3. Summary of transformities for Earth's major heat contributing radionuclides ^a

Isotope	T_G (gej J ⁻¹)	T_G Sunlight (gej j ⁻¹)	SER (seJ J ⁻¹)
⁴⁰ K	6.19	7.65 E-4	8.05 E3
²³² Th	3.18	7.65 E-4	4.16 E3
²³⁵ U ^b	2.93	7.65 E-4	3.84 E3
²³⁸ U	2.8	7.65 E-4	3.66 E3

a. From (Siegel et al. 2016)

b. Contribution to the GEB from ²³⁵U is very small.

Table 3-4. Summary of energies associated with Earth's accretion

Item	Symbol	Energy (E30 J)
Gravitational Potential	G_E	249
Earth Rotational KE	$K_{E,O}$	7.29
Earth Primordial Heat	$Q_{E,O}$	22.0

Table 3-5. Exergy, solar transformity and global empower contribution of the radio isotopes.

Isotope	(TW) ¹	Exergy (E20 J yr ⁻¹)	SER ² (seJ J ⁻¹)	Global solar equivalent energy contribution (seJ y ⁻¹)
³⁸ U	6.3	1.98	3.66 E3	7.24 E23
²³² Th	6.3	1.98	4.16 E3	8.23 E23
⁴⁰ K	3.1	0.99	8.05 E3	7.97 E23
Total	15.7	4.95	4.60 E3	2.34 E24

1. See section Radiogenic Heat Contributions
2. Solar equivalences are from Chapter 2

Table 3-6. Summary of solar equivalences for Earth rotational KE and primordial thermal energy.

Item	Symbol	Energy ¹ (E30 J)	Energy of Storage (E30 J)	T _G (gej J ⁻¹)	SER ² (seJ J ⁻¹)
Gravitational Potential	G _E	249		--	--
Earth Rotational KE	K _{E,O}	62	7.29	8.5	11,100
Earth Primordial Heat	Q _{E,O}	187	22	8.5	11,100

1. Proportion of original GPE allocated to rotational KE and primordial heat is according on current relative magnitude of the storage of KE compared with primordial heat.
2. Sunlight gravitational transformity = 7.65E-4 gej/J; therefore, solar equivalence ratio of rotational KE and primordial heat are computed by dividing gravitational transformity of each (T_G) by the sunlight gravitational transformity (T_S)

Table 3-7. Annual emergy contributions to Earth's geobiosphere using the split allocation.

Note	Source	Exergy (J y ⁻¹)	SER (seJ/J)	Annual solar equivalent flux (seJ/y)
	Sunlight	3.60 E24	1	3.60 E24
2	Primordial Heat	5.95 E20	11,100	6.62 E24
3	Radiogenic Heat	4.95 E20	4,740	2.34 E24
4	Tide Dissipation	1.17 E20	11,100	1.30 E24
	GEB			13.9 E24

Exergy of solar insolation is equal to 3.6 E24 J y⁻¹ (Brown and Ulgiati, 2016). By definition UEV of Sunlight equals 1.0 Primordial heat equal to 55% of total heat (34.6 TW), assuming average of ranges given in Table 5 Brown and Ulgiati, (2015). Primordial heat UEV from Table 3-6. Radiogenic heat equal to 45% of total heat (34.6 TW). Radiogenic UEV assumes average of SERs given in Table 3-5. Tidal dissipation is assumed equivalent to Earth rotational KE dissipated. Exergy of tidal input from Munk and Wunsch (1998). Tidal UEV from Table 3-6.

Table 3-8. Unit Energy Values, expressed as solar equivalence ratios, of the three main driving energies of Earth's geobiosphere.

Source	<i>SER</i> (seJ/J)
Sunlight	1
Geothermal ¹	8,240
Tide Dissipation	11,100

1. UEV is the weighted average of radiogenic and primordial heat

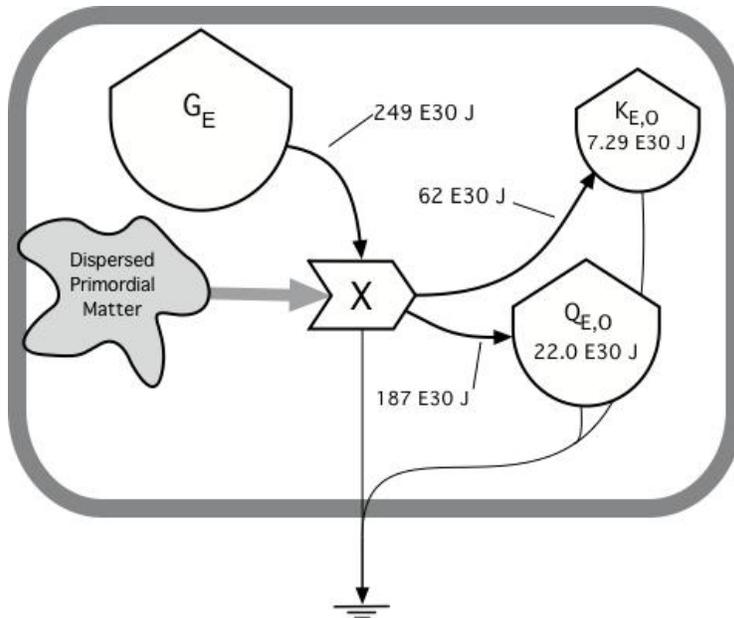


Figure 3-1. Aggregated diagram of the accretion process generating Earth's primordial heat ($G_{E,O}$) and rotational kinetic energy ($K_{E,O}$) (data from Table 3-4). The time frame for this analysis begins after the materials in the Earth's solar system have begun to form protoplanetary disks; therefore, the dispersed matter is shown as a cloudlike storage, rather than a source (from De Vilbiss et al. 2016).

Table 3-9. Five alternative configurations to assign gravitational potential energy to Earth rotational KE and primordial heat (from De Vilbiss et al., 2016).

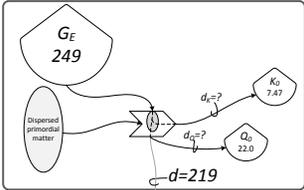
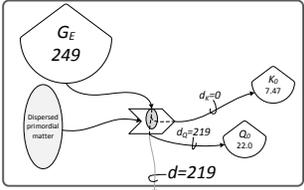
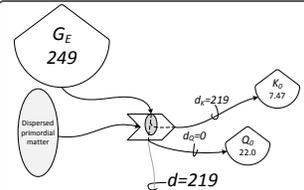
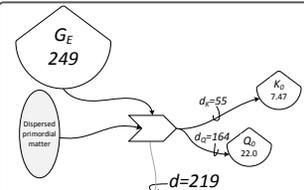
Method	Allocation of dissipation	Diagram	Mathematical effect	Pros	Cons
By-product (1)	Separately to rotational KE and primordial heat according to literature values for the efficiency of their production processes		$\tau_K \neq \tau_Q$ $\tau_K, \tau_Q > 1 \text{ gej}/J$	Additive. Most accurate representation of reality.	Values unknown.
By-product (2)	Total GPE assigned to primordial heat		$\tau_Q > \tau_K = 1 \frac{\text{gej}}{J}$	Additive.	Unfalsifiable analyst decision.
By-product (3)	Total GPE assigned to rotational KE		$\tau_Q = 1 \frac{\text{gej}}{J} < \tau_K$	Additive.	Unfalsifiable analyst decision.
Split	GPE of each flow is proportional to the exergy of each final storage.		$\tau_K = \tau_Q$ $\tau_K, \tau_Q > 1 \text{ gej}/J$	Additive. Most minimal analyst bias.	No quality distinction between heat and rotational energy.

Table 3-9. Continued

Method	Allocation of dissipation	Diagram	Mathematical effect	Pros	Cons
Co-product	Total GPE allocated to both outputs,	<p>The diagram shows an energy flow starting from a pentagon labeled G_E with the value 249. An arrow points from this pentagon to a trapezoidal shape labeled 'dispersed primordial matter'. From this trapezoid, two arrows branch out to two smaller pentagons: one labeled K_Q with the value 7.47, and another labeled Q_Q with the value 22.0. Below the trapezoid, there is a label $d=219$ with a downward-pointing arrow.</p>	$\tau_K \neq \tau_Q$ $\tau_K, \tau_Q > 1 \text{ gej/J}$	Most simplistic.	Co-products cannot be added.

Note that using the expression $GPE_o = G \frac{(m_E + m_m)}{2r}$ where G , m_E , and m_m are as defined above, and $r = 3.85 \text{ E}8 \text{ m}$ is the semi-major axis between Earth and Moon, and the rate of orbital recession is $dr/dt = 3.82 \text{ cm yr}^{-1}$ (Williams, 2000), the rate of change of orbital gravitational potential energy is $dGPE_o/dt = 0.24 \text{ TW}$. This value is approximately 6.4% of the total tidal braking of the Earth which is 3.7 TW. Hence 93.6% of the dissipation of Earth's rotational kinetic energy dissipates as heat, facilitated by tidal friction. 96% of tidal braking occurs in the ocean, hence about 90% of Earth's rotational deceleration results in heat in the oceans. What we here compute is a gravitational transformity, and solar equivalence ratio, of Earth's despin. 9/10ths of the energy of this despin becomes ocean tides and eventually heat. For this reason, we accept that our SER for Earth's despin to approximate the solar equivalence of ocean tides.

CHAPTER 4 NEW METHOD TO COMPUTE THE EMERGY OF CRUSTAL MINERALS

Prior Studies

This Chapter examines the emergy of Earth's crust and crustal minerals. To begin we must understand that sunlight is the most practical unit for accounting emergy on Earth because of at least two reasons. One is that it is the most abundant and evenly distributed exergy source to the Earth system. And two it is a common denominator to the genesis of more energy and material circulations on Earth than any other Earth exergy source. Thus Earth emergy is expressed as solar emergy. The other important independent exergy sources to the Earth are explained in Chapter 3.

The GEB is the sum of Earth's exergy inputs, expressed as equivalent sunlight exergy. After reevaluation of the exergy sources driving the geobiosphere, following the 8th Biennial Emery Conference, the GEB was established as 12.0 E24 seJ/yr (Brown et al., 2016) and this is the GEB used in this Chapter.

The following definitions come into use throughout Chapter 4. When concentrated materials disperse to background concentrations heat and entropy are generated (Faber, 1984). In other words, a concentration gradient is a storage of available potential energy (exergy). Thus concentrated minerals in Earth's crust possess exergy. The emergy of such concentrated minerals is the cumulative exergy of one form dissipated to create it. In the case of Earth's crust, the cumulative exergy dissipated in its formation is the GEB over a certain period of time. And for any given mineral, or for the crust overall, the emergy of the unit divided by its exergy is called transformity (sej/J).

This chapter was previously published in Ecological Engineering by C. De Vilbiss and M.T. Brown (2015). Some changes are made here that are different from the publication. Received permission to republish.

Transformities can be perceived on a hierarchy of energy quality (Odum, 1996) in the geobiosphere. Quality indicates the donor-, or supply-side, perspective (i.e. what is required from the environment for genesis) of an exergy's ability to induce useful work (utility) in the geobiospheric system (Odum, 1996). A storage's emergy divided by its useful mass is called specific emergy (sej/g). Specific emergy indicates material quality and is linked to transformity via specific exergy (J/g). Specific emergy and transformity, by definition, jointly characterize resource quality. They are collectively referred to as UEVs (unit emergy values).

A driving question for this research is how to relate crustal mineral specific emergy to changes in concentration and changes in specific exergy? Presently crustal mineral emergy is accounted by mass, rather than by exergy, because mined materials are accounted by mass in the literature, and mass is easier to handle with available emergy computation methods. Flaws of these methods will be discussed next, after which we propose several calculation procedures for crustal mineral UEVs. Lastly we apply these new UEVs to the emergy accounting of the US economy's mineral consumption in 2008 and compare the results with previous analyses.

Previous Estimates of Crustal Mineral Emergy

Various tectonic (Odum, 1996, Table 3.3) and sedimentary processes (Odum, 2000a, Table 10) have been evaluated as co-products of the GEB. Co-product assumption is like a black-box where the internal pathways of crustal genesis are unknown. The source exergy is attributed to each output (there are several). Co-products embody the same source exergy and so their emergy should not later be added together to avoid double counting the source. The emergy of sedimentary (e.g. limestone, evaporites) and tectonic rocks (e.g. granitic, metamorphic, etc.) represents

the embodiment of past dissipated exergy. In fact, according to the computation of both (Ibid.) the sedimentary and tectonic rocks embody the same past dissipated exergy (the GEB). The dual embodiment of the GEB within evaporates and tectonic rocks has raised a question of whether the source exergy is double counted when adding the emergy of these rocks together.

On one hand are proponents of the idea that the emergy of sedimentary and tectonic rocks are additive because in reality the rocks were produced in the Earth system at different times and places, i.e. that no two rocks actually utilized the same exergy during their formation. Those proponents assert that the emergy algebra rules are applied differently in the computation of UEVs compared with landscape accounting (e.g. a nation) or from small scale processes. For example, the renewable energies of a region are contemporaneous flows, i.e. Sun makes rain and wind, wind drives rain, etc., in which case we account only the largest of the secondary flows compared with the sum of tripartite flows into that region. However, in the computation of a global UEV for tectonic vs. sedimentary rocks the genesis time merely partially overlaps. Also due to the intractability of allocating exergy dissipation within the geologic system, a generalization is utilized to attribute all the GEB to both, knowing that there is in fact no real double utilization of exergy in rock formation. Because the rocks were definitely formed using different exergy, their emergy is additive. That is, though the UEV for each rock is computed using the same emergy, the reality is that they are not co-produced at the same time/space and therefore can be added.

On the other hand, are proponents of the idea that the emergy of sedimentary and tectonic rocks are co-products which should not be added to avoid double counting

the source exergy. In the mathematics of how the UEV is calculated the GEB is progenitor of both tectonic and sedimentary rocks. The total emergy of the annual genesis of both kinds of rocks equals the GEB. Taken separately, the total emergy of annual production of sedimentary rocks plus the total emergy of annual production of tectonic rocks would equal two times the GEB. It must be emphasized that we are simply considering the annual production of these rocks because that is how their UEV is calculated (e.g. total rock mass on Earth divided by average rock age equals annual production). To add these two rocks' emergy doubles the emergy of the system simply because the analyst divided the resource into two kinds of rocks, attributed the planet's emergy budget to both, and then considered them to be additive. A more simplistic view with only one kind of rock would avoid this situation but with over simplification as a consequence. A more detailed view would categorize many more kinds of rocks, complicating the situation given above but also better representing the diversity of rocks in the actual system. So, when accounting the total global rock production, it clearly inflates the global emergy to consider each rock's emergy to be additive in the way it has been calculated (which is a co-product method). However, we might never actually account the total annual rock production in any realistic evaluation. As we reduce the quantity of rock we account (lowering it from total global flux down to a national annual consumption rate, which is a small fraction of geologic flux) the amplification of overall system emergy becomes less obvious. At these small consumption levels (relative to annual Earth production) the amplifying effect of double accounting becomes more difficult to observe. Here, proponents assert that emergy algebra rules should apply to all scales, time and space. If we consider it double counting when adding the emergy of

the total of Earth's resources together it would also be double accounting to add the energy of some of Earth's resources together, given their UEVs were computed as co-products with the same source exergy, namely the GEB.

Mass Enrichment Method

Odum (1999, 2000b) estimated a linear relation between the specific energy of lead (Pb) and its concentration. This relation results from topological energy methods (i.e. ore grade was assumed to be linearly related to the energy of ore body creation). Topological energy enrichment was extended to all crustal elements (Cohen et al., 2007) and validated against computed economic relationships to ore grade. Mined copper ore tonnage was negative \log_{10} correlated with ore grade, a phenomenon consistent across crustal elements (Ibid.). Thus ore body specific energy (for all crustal elements) was assumed linearly related with purity. This mass enrichment (ME; Ibid.) method is the most commonly applied method to compute the energy of crustal materials (e.g. Rugani et al., 2011; Brown et al., 2009) but a thermodynamic relationship between mass and exergy, and thus specific energy and transformity, is missing.

Most resources in energy accounting possess both a transformity and specific energy. All resources have the potential to be expressed as both specific energy and transformity although this is impractical in many cases. For example we could consider the mass of Sunlight or the mass of water carrying wave energy and from this compute a specific energy for these resources. This assertion is not readily evident because many resources are almost always expressed as either a transformity (e.g. sunlight, wind, fossil fuels, etc.) or specific energy (e.g. metals, minerals, fertilizers, lumber, etc.). It's possible, though impractical, to express sunlight as mass or fertilizer as chemical exergy which makes possible the expression of their specific energy or transformity

respectively. All transformities are the ratio of a resource's emergy to its exergy (either chemical, gravitational, kinetic, thermal, radiation, etc.). It is the dissipation of exergy, which carries materials along the energy hierarchy where such materials organize into material hierarchies (Odum, 1999). Thus exergy links the energy and material hierarchy, represented by transformity and specific emergy respectively. The general relationships are as follows:

$$\tau = \varepsilon / \beta \quad (4-1)$$

$$\varepsilon = \tau \cdot \beta \quad (4-2)$$

$$\beta = \varepsilon / \tau \quad (4-3)$$

Where transformity, τ (sej/J), is linked to specific emergy, ε (sej/g), through specific exergy, β (J/g). A linear relation between specific emergy and transformity is possible only if specific exergy is a linear function. As shown in two sections from now specific exergy of minerals is a non-linear function of molecular purity. Thus, for minerals, transformity and specific emergy are not linearly related.

Emergy of Material Inputs to US Economy

Table 4-1 shows the major material inputs to the US economy in 2008 (see Sweeney et al, 2007 for explanation). The emergy of the 2008 US economy was dominated by limestone or items whose UEV is approximated to limestone¹. Due to this fact any change in the emergy of limestone greatly effects the overall emergy of the nation. Actually limestone is not principally a geologically mediated mineral but rather it is biogenic in origin. Thus we'll present another method for computing the emergy of

¹ Average crustal specific emergy has changed due to updated values for the mass of the crust and its generation time.

limestone which is independent of the overall minerals method that is the subject of this Chapter.

Emergy of Limestone

Up until now the limestone UEV was 9.5 E9 sej/g (Odum, 2000; Table 10) on a $15.83\text{e}24 \text{ seJ/yr}$ baseline and by assuming it as a co-product of the land cycle (18% of land cycle). Thus average crust (Ibid.) 1.69 E9 sej/g divided by 18% is $9.5\text{e}9 \text{ sej/g}$. Consequently, when any land cycle co-products (e.g. sediment, shale, sandstone, evaporites, limestones, etc.) are accounted in an emergy table, only the largest should be considered to avoid double counting. The new average crust specific emergy (1.38 E9 sej/g ; see next section) results in a limestone UEV of 7.8 E9 sej/g using Odum's method.

The only other emergy evaluation of calcium carbonate (limestone) is from McClanahan (1990). He evaluates a couple of protected coral reefs which deposit CaCO_3 at a rate of about $2,221 \text{ g/m}^2/\text{yr}$. Updating transformities for his evaluation results in an areal empower of $6.39 \text{ E}13 \text{ sej/m}^2/\text{yr}$ in which ocean currents are the largest emergy contributor. This yields a limestone UEV of $2.88 \text{ E}10 \text{ sej/g}$ similar to Odum's land cycle co-product value for limestone. Compare this with the limestone UEV as part of the crustal cycle (i.e. abiotic production) of $3.28 \text{ E}7 \text{ sej/g}$ (De Vilbiss and Brown, 2015). McClanahan's research data is very useful. Some tweaks are needed to utilize his data due to computation errors in his document. The methods of these updates are described in the methods section.

Average Crustal Specific Emergy

The GEB drives, among many things, the cycling and concentration of crustal minerals. Crustal cycling is driven from below by the geothermal engine and from above

by the solar and tidally driven erosive forces (Odum 2001). In more recent geologic time biologically dominated processes have contributed to crustal erosion.

The generation of crustal material involves emplacing new magma from the mantle. Gross crustal growth appears to have always been about $3 \text{ km}^3/\text{yr}$ but by circa 3 Ga recycling brought net growth to zero (Cawood et al., 2013). Probably this is when modern plate tectonics initiated subduction (i.e. crustal recycle).

Earth's crust embodies billions of years of the GEB. During this time the GEB is assumed constant because the Earth's geodynamic history is not fully understood (e.g. the rate of Earth's cooling; Dobretsov, 2010, or tidal friction due to varying ocean volume and continental exposure; Korenaga, 2013). Thus details of crustal genesis and details of a dynamic GEB are not considered (Figure 4-1). Also fossil fuel formation is excluded. Our model shows the modern general material flow from continents to the oceans via the effects of Sunlight and tidally driven erosive forces. Subduction reassembles continents or separates the crust into the mantle. Ocean drains into the mantle mostly by hydrothermal circulation and some by subduction (Rea and Ruff, 1996).

To estimate the average steady-state specific energy of the general crust mixture we only need the GEB (assumed constant) along with average replacement time (2.4-2.5 Ga; Taylor and McLennan, 1995; Veizer and Jansen, 1985) of the considered mass of the continental crust. Using the upper limit age, the energy of the continental crust is the product of crustal age and the GEB (i.e. $2.5 \text{ E9 yr} * 12.0 \text{ E24 seJ/yr} = 3.0 \text{ E34 seJ}$).

Earth is practically closed-to-matter so its elemental endowment is fixed. Though the composition of lower crust is difficult to establish (Korenega, 2013) we distinguish crust from the underlying mantle due to phase difference and chemical enrichment of certain elements e.g. U, Th, and K in the crust (Huang et al., 2013). Additionally, oceanic crust differs greatly from continental crust. Continental crust is about ten-times older, five-times more massive, less dense and composed mostly of granites compared with the denser basalts that compose the major part of oceanic crust. Although mineral mining may take place in the oceanic crust in the future, there is a definite compositional difference between oceanic crust and continental crust (Valero, 2008). For these reasons we consider the continental crust to be hierarchically (as well as in elevation) higher than oceanic crust and so the UEV for crust will only account the mass of the continental crust, which is $2.171 \text{ E}25 \text{ g}$ (Peterson and Depaolo, 2007). Average crustal specific emergy is thus the ratio of crustal emergy to crustal mass

$$\bar{\epsilon} = 2.5 \text{ E}9 \text{ year} \times 12.0 \text{ E}24 \text{ seJ/yr} \div 2.171 \text{ E}25 \text{ g} = 1.38 \text{ E}9 \text{ seJ/g}.$$

Chronosequence of Methods Considered and Dismissed: Chemical and Concentration Exergy

Martinez et al. (2007) argued for the exergeocology method rather than the emergy method. They focused on the chemical and concentration exergy of minerals. Mineral chemical exergy expresses the minimum work required for chemically combining the reference substances dispersed in the RE (reference environment, Szargut et al., 2005; Valero, 2008). The RE represents a “dead” planet whose chemistry has fully reacted, dispersed, and mixed.

The chemical composition of the RE is fixed by the natural environment (Valero, 2008). For each element the most abundant molecule which contains that element, and

which also possesses a Gibb's formation energy within a 'stable' range, is classified as a reference substance. This is known as Szargut's criterion of partial stability (Szargut et al., 2005) and it generates some negative chemical exergies for many minerals more stable than reference substances (Table 4-2). The negative chemical exergies lead to skepticism about the chosen RE. However, this RE is preferable to others whose resulting dead planets don't resemble Earth (see discussion in Valero, 2008).

It's theoretically inconsistent in the emergy theory to have a negative UEV. Zero is the smallest UEV representing the quality of zero potential energy. Just as there is no sub-zero Kelvin, UEVs indicate quality on an absolute scale. However, as mentioned above, negative chemical exergies for some minerals are unavoidable with current methods. To utilize chemical exergy as a denominator in mineral transformity we use absolute values. But first we address the concept of an average chemical crustal transformity.

Average crustal transformity

Chemical exergy b_{ch} for a mineral body is the sum of the standard chemical exergy $b_{ch,i}$ and mixing exergy $RT_0 \ln x_i$ for each constituent mineral i according to their molar fractions x Eq. 4-1. Note the similarity of Eq. 4-1 to the Gibb's free energy Eq. 4-2. Gibb's free energies, however, are negative for all crustal minerals (Valero et al., 2012).

$$b_{ch,solution} = \sum_{i=1}^m x_i \cdot (b_{ch,i} + RT_0 \ln x_i) \quad (4-1)$$

$$\Delta G_{f,solution} = \sum_{i=1}^m x_i \cdot (\Delta G_{f,i}^0 + RT_0 \ln x_i) \quad (4-2)$$

The emergy of concentrated minerals is the past dissipated exergy which carried a mineral from average abundance to its more concentrated state. This emergy is the GEB over the age of the crust (3 E34 sej). The chemical exergy of the upper continental

crust is the application of Eq. 4-1 to all crustal minerals given in Valero et al. (2012), which is 366.56 kJ/mole or 2,324 J/g crust (157.7 g/mole average crust). The average chemical transformity for upper continental crust is the ratio of average crustal specific energy (1.38 E9 sej/g) to average chemical exergy (2,324 J/g) which is $\bar{t}_{crust} = 5.94 \text{ E}05 \text{ sej/J}$.

This number expresses that each joule of chemical exergy, regardless of parent mineral, has the same quality (i.e. transformity). Also, as demonstrated later, this number is fixed such that as concentration changes, and so also as specific exergy changes, transformity does not, because we have no formulation to do so. Despite these drawbacks, average crustal chemical transformity is promising as seen in the Results section.

Energy needed to concentrate vs. concentration exergy

Concentration exergy is a prevalent concept in the emerging field of exergoecology and so clarity between the concept of concentration exergy vs. the energy needed to concentrate is necessary to either use or dispel either. The property of concentration might appear more useful than chemical potential to underscore mineral quality, however the following will demonstrate how common descriptions of the property of concentration do not succeed for our purposes. If the reader wishes to advance to our most successful methods of determining mineral energy please see Methods section.

Faber (1984, Faber et al., 1987) describe the minimum energy needed to separate a substance in an ideal mixture. They assume volumetric fraction equals molar fraction (i.e. that every kind of molecule occupies the same volume; Eq. 4-3). $\beta_{i,c}$ is the

external energy needed to concentrate, expressed in J/mole, where R is the gas constant, T is absolute temperature, and x is the molar fraction (mole/mole) of mineral i at concentration c . The energy needed to concentrate goes to zero at purity and to infinity at miniscule concentrations.

$$\beta_{i,c} = -RT \cdot \left[\ln x_{i,c} + \frac{(1 - x_{i,c})}{x_{i,c}} \cdot \ln(1 - x_{i,c}) \right] \quad (4-3)$$

Later, several papers (Valero and Valero, 2012; Valero, 2008; Valero et al., 2008) use Eq. 4-3 to describe concentration exergy which is incorrect. Eq. 4-4 [units J/mole] is in fact concentration exergy defined as the magnitude of energy needed to concentrate (to complete purity) from average abundance minus the magnitude needed to concentrate from the mine purity (Eq. 4-4).

$$b_{i,c} = \beta_{i,c} - \bar{\beta}_i = RT \cdot \left[\ln \frac{\bar{x}_i}{x_{i,c}} + \frac{(1 - x_{i,c})}{x_{i,c}} \cdot \ln(1 - x_{i,c}) - \frac{(1 - \bar{x}_i)}{\bar{x}_i} \cdot \ln(1 - \bar{x}_i) \right] \quad (4-4)$$

Note the y-axis in Figure 4-2 differs from previous authors who thought it to be in units of kJ/mole. Figure 4-2 displays the concentration exergy, a concept which has been used to describe mineral exergy value and also mineral emergy (Jamali-Zghal et al., 2014). It is relevant here to explain the fallacy in that method so we can dismiss and move on.

Valero et al. (2008) combines chemical and concentration exergy to characterize the natural capital of minerals. However, concentration is already accounted in the mixing term for chemical exergy (see Eq. 4-1). To add concentration and chemical exergy double counts the exergy of concentration of a mineral.

Concentration exergy references only mineral abundance, and is therefore the same for any mineral whose concentration parameters are identical to another mineral (i.e. concentration exergy is not unique to any particular mineral, unlike chemical exergy

or Gibb's formation energy). Further a mineral can have negative concentration exergy if its concentration is below average, but we cannot have a negative transformity.

Whereas a negative chemical exergy value results from the analyst decision of which substances in a mixture will be the reference substance, concentration exergy is more objective and is determined only by the concentration parameter of a substance within a mixture. Thus a negative concentration exergy literally means the substance will tend to become more concentrated through time as the system mixes, whereas a negative chemical exergy value means the mineral will spontaneously form, and is subject to the decision of which substances to consider as reference substances.

Later we make use of negative chemical exergies because they are the result of a chosen reference environment. However negative concentration exergy is unavoidable regardless of analyst choice. The amount of material below average concentrations equals the amount above average concentrations (a mathematical truism). Thus globally the continuous flux of crust produces essentially no net concentration exergy. It is therefore impossible to have a global transformity for crustal concentration exergy.

Due to the aforementioned issues De Vilbiss (2013) used concentration energy Eq. 4-3 rather than concentration exergy Eq. 4-4 to link crustal mass quality with energy quality. The energy needed to concentrate (different from concentration exergy) was a useful formulation because energy needed to concentrate is a continuous function from zero abundance (infinity energy needed to concentrate) through to purity (zero energy needed to concentrate). The smaller the energy needed to concentrate, the higher its inverse, thereby quantitatively indicating a more concentrated substance to have higher

quality which aligns with the presupposition of Cohen et al. (2007) and Odum (2001). The ratio of the energy needed to concentrate at average abundance to the energy needed to concentrate at the mine abundance indicated a 'transformity' enrichment factor from which specific emergies were calculated.

That method was not desirable except in the absence of any other thermodynamic method in the literature to link crustal specific energy with its transformity. It was considered an improvement, but suffered from the fact that energy needed for concentration is not exergy and therefore a transformity, strictly speaking, cannot be yielded from the ratio of emergy to concentration energy. The link between transformity and specific energy was still missing.

Adding concentration exergy with chemical exergy

We invest time to explain the differences between emergy and exergoecology because all the mineral data in Chapter 4 (chemical exergies, Gibb's formation energies, mineral abundance, and reference environment) are taken from exergoecology publications. However useful this data is, we must be clear on the differences in methods and why some of their methods are used and others not.

In the emergy method summing exergies of different resources implies they're exergy is of the same kind (i.e. they have the same quality/transformity). Energies are added only if they're the same kind. In most cases they are converted into emergy units and their emergies are added. This idea of adding exergies only if they are like kind is different in exergoecology. In exergoecology some researchers sum concentration and chemical exergy to indicate resource capital. To add concentration exergy with chemical exergy misaligns with the emergy philosophy as explained next.

The reference datum differs for chemical exergy vs. concentration exergy. Though similar, concentration exergy is the gradient of a molecule's abundance relative to its average abundance in the crustal soup. Chemical exergy however results from the deviation of chemical composition of a material from the [aggregate] composition of the commonly appearing components of the RE (Szargut, 1989). Different reference frames connote different kinds of exergy, which, in the energy method, may be added only after conversion to a common unit (e.g. sej). We don't yet know how to partition Earth's environmental support among the genesis of chemical exergy and concentration exergy of mineral bodies. Thus we have yet the knowledge to compute separate energy values for concentration vs. chemical exergy of the crust.

According to Eq. 4-4 minerals below average crustal abundance have negative concentration exergy. From this initial condition the concentration process would be endothermic, and thus doesn't drive work. Negative depends on the reference datum. If we consider only minerals above their average crustal abundance, chemical exergy still out measures concentration exergy except for minerals with very small chemical exergies that are also highly concentrated. For example, the chemical exergies of Colemanite and Orthoclase/K-feldspar (Table 4-2) are more negative than any amount of possible positive concentration exergy can negate (even in a pure deposit). Therefore, even summing chemical and concentration exergy for these minerals, negative exergy is unavoidable, although it's magnitude would be reduced. For some others the sum total exergy would become positive. Keep in mind that negative chemical exergy results from the 'choice' of reference substances (Szargut, 1989). Thus is not necessarily true that when concentration and chemical exergy are added for a

mineral, that negative means endothermic and positive means exothermic. Adding chemical and concentration exergies muddies the understanding of each.

Concentration exergy characterizes the heat generated upon molecular dispersal. Chemical exergy, on the other hand, characterizes the heat of sub-molecular (electron) chemical equilibration. Adding chemical and concentration exergies is analogous to summing thermal and kinetic exergies. While, in principle, thermal and kinetic exergy both are a function of velocity (thermal being molecular scale velocity and kinetic being macro-molecular velocity), the energy of a wind gust accomplishes different work (in the geobiosphere) than an equal measure of atmospheric thermal gradient. The emergy method presupposes the exergy of wind and temperature are additive only after being expressed in a form of energy common to both their geneses (e.g. sunlight). It is methodologically inconsistent, in the emergy method, to sum concentration and chemical exergy because they refer to different kinds of potentials.

Jamali-Zghal et al. (2014) made the first attempt to integrate chemical exergy into mineral emergy computations. They characterized mineral value with the combination of chemical and concentration exergy along with mineral exergy replacement cost, which is the exergy required to remake the properties of a mineral deposit by means of human technology. Mineral exergy, in this way, is defined as the minimum energy required to remake a deposit from the reference environment (RE) via a reversible anthropogenic process. While a brave first attempt there are still many flaws. For example, the average transformity of the crust was determined to be the weighted average transformity of Earth's tripartite (Table 1, *Ibid.*). As shown already average crust transformity (sej/J) is the emergy of the crust divided by the exergy of the crust. Further,

those authors summed a mineral's exergy replacement cost with its intrinsic chemical and concentration exergies. Mineral exergy replacement cost is a measure of human investment needed to remake an ore deposit, which is far from optimum as evidenced by humanity's rapidly evolving technological efficiency. Exergy replacement cost is not a characteristic held by the mineral itself and therefore adding it to a mineral's chemical and concentration exergy fallaciously inflates a mineral's potential to do work (i.e. its exergy).

Methods

Before continuing, note we reject summing chemical and concentration exergy because they reference different datum (see previous sections).

Unique Mineral Transformities

Now consider that each mineral has a unique chemical transformity (Eq. 4-5), which is the ratio of average crust specific energy $\bar{\varepsilon}$ to the absolute value (because we can't make use of negative transformities) of a mineral's chemical exergy at its average crustal abundance.

$$\bar{\tau}_{ch,i} = \bar{\varepsilon} / |\bar{b}_{ch,i}| \quad (4-5)$$

Unique Gibb's transformities are found similarly (Eq. 4-6).

$$\bar{\tau}_{\Delta G,i} = \bar{\varepsilon} / |\Delta \bar{G}_i| \quad (4-6)$$

Minerals are accounted by mass. Hence we need to convert our transformities (energy/exergy) to specific energies (energy/mass). Mineral specific energy at the mine ε_i is computed as the product of transformity τ and either chemical exergy at the mine (Eq. 4-7) or Gibb's formation energy at the mine (Eq. 4-8).

$$\varepsilon_i = \bar{\tau}_{ch,i} \cdot b_{ch,i} \quad (4-7)$$

$$\varepsilon_i = \bar{\tau}_{\Delta G,i} \cdot \Delta G_{ch,i} \quad (4-8)$$

Accounting Only Mixing Exergy

The previous section shows computation for two kinds of mineral transformities, chemical exergy and Gibb's transformities. However, the Gibb's formation energy is, just as its name suggests, the energy needed to form the mineral under standard conditions. This is actually very similar to energy (i.e. the exergy dissipated to create something). However, when the mineral is concentrated it possesses a different formation energy as the chemical conditions around it have changed, namely itself is more abundant. The difference in the formation energy at the mine to the formation energy at average conditions is called mixing exergy.

Note Gibb's (Eq. 4-2) and chemical exergy (Eq. 4-1) have identical mixing exergy terms (the second part of those equations). Though that we account the total chemical exergy as the chemical exergy characterizes the full potential of the mineral to do work on the system. With Gibb's formation energy we also want the value of what can do work on the system, which is characterized by its mixing exergy as described above.

Mixing exergy (not to be confused with concentration exergy) refers to the difference in Gibb's energy ($\Delta G_{mine,i} - \Delta \bar{G}_i = RT \ln \frac{x_{i,mine}}{\bar{x}_i}$) between mine and average crustal conditions. The specific energy of minerals at the mine (ε_i) accounting only mixing exergy is the product mixing exergy $RT \ln \frac{x_{i,mine}}{\bar{x}_i}$ with its Gibb's transformity (Eq. (4-9)).

$$\varepsilon_i = \bar{\tau}_{\Delta G,i} \cdot RT \ln \frac{x_{i,mine}}{\bar{x}_i} \quad (4-9)$$

Average Crustal Chemical Exergy Transformity

In the introduction we showed how to calculate the average crustal transformity using chemical exergy as a base (5.94 E5 sej/J). However, what good is an average chemical exergy transformity? As the mineral is concentrated its exergy density (J/g) increases. As mineral concentration and exergy density increases so too must mineral transformity as with all resources which require more environmental support to concentrate. However, as we will see with all the transformities presented here, transformity is not formulated to change with purity. What is formulated to change is exergy density (J/g) and specific emergy (sej/g). These two values change with purity, but not transformity. For all the methods presented, either transformity or specific emergy must be held constant. This is undesirable yet unavoidable. In this case average crustal transformity is held constant.

As with unique mineral chemical exergy transformities, for average crustal chemical exergy transformity the total exergy is accounted, not just the mixing exergy (Eq. 4-10).

$$\varepsilon_i = \bar{\tau}_{crust} \cdot b_{ch,i} \quad (4-10)$$

Method to Compute the Emergy of Limestone

The following describes the updates made to McClanahan's (1990) study of a coral reef system in order to compute the emergy of limestone. McClanahan assumed 10% absorption of ocean kinetic energy. Rosman and Hench (2011) found the proportion of ocean kinetic energy dissipated as it drags over, under, around, and through coral reefs ranged from 0.015 to 0.8, with a modeled average of 0.0823.

Some of McClanahan's energy equations needed modifying as their solutions yielded incorrect units for their implementation. Correcting for these, using all the same

data from his research, alters the outcome of his evaluation. Ocean currents no longer are the dominant energy source. Waves, closely followed by tides, characterize his reef system. Additionally, McClanahan didn't estimate the percent absorption of tides or waves. Wave energy dissipation for reef platforms similar to McClanahan's system (including nearly identical ocean current velocity) is about 15.2% (Nelson, 1996).

Nuclear Energy of Mined Uranium

The SER of Uranium-238 is $3.66 \text{ E}3 \text{ seJ/J}$ (Table 2-5). Also each atom of Uranium-238 emits 47.7 MeV ($7.64 \text{ E}-12 \text{ J/atom}$) of energy upon its decay to a stable isotope (Chapter 2). The specific energy of ^{238}U is:

$$\varepsilon_{238\text{U}} = 3.66 \text{ E}3 \frac{\text{seJ}}{\text{J}} \times 7.64 \text{ E}-12 \frac{\text{J}}{\text{atom}} \times 6.02 \text{ E}23 \frac{\text{atom}}{\text{mole}} \div 238 \frac{\text{g}}{\text{mole}} = 7.07 \text{ E}13 \text{ seJ/g}$$

In 2008 the US internally mined and consumed 1,501 metric ton of the metal Uranium (NEAD). The energy contribution of Uranium to the 2008 US economy was $7.07 \text{ E}13 \frac{\text{seJ}}{\text{g}} \times 1,501 \frac{\text{MT}}{\text{yr}} \times 1 \text{ E}6 \frac{\text{g}}{\text{MT}} = 1.06 \text{ E}23 \text{ seJ/yr}$.

Note that this quantity assumed all the nuclear exergy of uranium is used during the fission process, which is false since we bury the product underground due to it retaining some radiation. This assumption should be modified in the future to reflect the actual exergy dissipated during the human induced fission process.

Results

For the ten largest mineral energy contributors to the US economy the Gibb's transformities range two orders of magnitude and the chemical transformities range four orders of magnitude (Table 4-3). The crustal average chemical transformity is not shown in Table 4-3 because it is a constant value for all minerals and all concentrations

(hence its name). The presupposition that rarer minerals possess higher UEVs will guide our decision toward the most appropriate method here.

With crustal average transformity held constant, we look for a relationship between average crustal abundance and mineral transformities using the chemical exergy and the Gibb's transformities. We presuppose there to be a negative relation such that more common minerals have lower transformities. Figure 4-3 shows no relationship between the unique mineral transformities (both Gibb's and chemical exergy) and mineral abundance where all trend line relations yielded very low R^2 values.

Similarly, we can look for a relationship between average crustal abundance and mineral specific energies for all three methods (Figure 4-4). We convert all mineral transformities into specific energies and test the relationship between mineral abundance and specific energy for the three methods as described in Table 4-5.

Plotting specific energy vs. average abundance of the mineral (for 20 non-limestone minerals for which we have transformities from NEAD) we expect to find a negative correlation in an accurate method. That is, a method that accurately represents reality would generally characterize abundant minerals with lower specific energies and rare minerals with higher specific energies. This negative relation is present for all but mostly for Gibb's transformities $R^2 = 0.45$ and average crustal transformity $R^2 = 0.20$ (Figure 4-4). According to this result Gibb's transformities are most promising.

The specific energies for the 20 minerals examined using the crustal average chemical exergy transformity range from $5.75 \text{ E}7 \text{ sej/g}$ (zircon) to $4.58 \text{ E}10 \text{ sej/g}$ (zinc).

With the Gibb's transformities accounting only mixing exergy the values range from 3.39 E6 sej/g (phosphate rock) to 4.72 E10 sej/g (silver).

The emergy of limestone

Updating McClanahan (1990) as described in the methods section results in coral reef areal empower of 3.69 E12 sej/m²/yr; Table 4-5. The ratio of this areal empower to calcite deposition rate in the study cite is 1.66 E9 sej/g (Table 4-6) which is just 17% of the 9.5 E9 sej/g used in NEAD.

$$\bar{\epsilon}_{CaCO_3} = 3.69 \text{ E12 sej/m}^2/\text{yr} \div 3.5 \text{ kg/m}^2/\text{yr} = 1.66 \text{ E9 sej/g}$$

Discussion: US Mineral/Metals Emergy

Table 4-4 gives the specific emergies for the ten most prominent mineral/metal inputs to the USA economy in 2008 (NEAD, 2012). The first column displays NEAD UEVs (updated using new average crustal specific energy), which utilize the ME method. In the next three columns' UEVs were calculated using 1) Gibb's transformity accounting mixing exergy; 2) chemical exergy transformity accounting total exergy; and 3) crustal average transformity accounting total chemical exergy.

In NEAD, limestone, dolomite, and gypsum all were assumed to have the UEV of limestone. We have continued this assumption. Of the other seven minerals (of the top ten contributors) note that the use of chemical exergy transformities unique for each mineral ascribe the highest transformity to the more common mineral (iron ore, zinc) and lower transformity to the rarer minerals of lead and cadmium. This is counter to the emergy presupposition that generally common resources have lower transformities than rarer resources in hierarchically organized system.

To examine the efficacy of these new methods for computing the emergy of minerals we use them to update the emergy driving the 2008 US (NEAD, 2012). The NEAD makes use of the mass enrichment (ME) method (Sweeney et al., 2007 and Cohen et al. 2007) to compute material UEVs. Concentrated non-renewables were 54% of total US emergy use in 2008 (Figure 4-5a), of which minerals and metals represented 52% (Figure 4-5b); thus about 27% of the total US emergy support is from minerals/metals, about 90% of which is limestone.

Using chemical exergy or Gibb's formation energy to compute the emergy of limestone is like computing the emergy of lumber using the chemical exergy of its carbon (i.e. limestone is mostly a biogenic rock). Correcting NEAD for the new average crustal specific emergy ($1.38 \text{ E}9 \text{ sej/g}$) reduces the total emergy contribution from minerals and metals to $8.22 \text{ E}24 \text{ sej/yr}$ where limestone still represents 90% of this total.

The last rows in Table 4-4 show the total US emergy in 2008 using just the top ten mineral contributors (98.88 % of total mineral/metal contribution) with our three potential methods. These values range from $1.64 \text{ E}24 \text{ sej/yr}$ (Gibb's mixing exergy method) to $8.96 \text{ E}24 \text{ sej/yr}$ using chemical exergy transformities. The percent contribution from limestone ranges from 18% of the total mineral/metal emergy (chemical exergy transformities accounting total exergy) to 97.17% (Gibb's transformities accounting just mixing exergy). The percent contribution from limestone is so high for Gibb's mixing exergy method because all minerals other than limestone have relatively small UEVs. Even if some mineral's UEVs are comparable to the limestone UEV the quantity of calcite mined each year dwarfs the other minerals. The overall

change in total mineral/metal energy compared with the original NEAD value ranges from 16.3% (Gibb's mixing method) to 89% (chemical exergy method).

Final Proposition

Undeniably the most acceptable results from this work are 1) the updated average crustal specific energy which reduces the mineral/metals energy of the US by about 18%; 2) the new biogenic UEV for limestone which reduced the energy contribution of limestone (which was 26% of the total US energy metabolism) by about 83%; and 3) the new nuclear energy contribution calculated from Uranium-238 consumption. If we only account for these three notable modifications, we may call this proposition 1.

Proposition 2, 3, and 4 include all the modifications from proposition 1 above, and additionally update the energy of all the other crustal minerals with the methods of crustal average chemical exergy transformity accounting total exergy (2), chemical exergy transformities accounting total exergy (3), and the Gibb's transformity method accounting only mixing exergy (4). A pie chart perspective on these four propositions (Figure 4-6) graphically shows that now the fossil fuels greatly outweigh the other non-renewable resources with limestone a distant second in all but for Proposition 3. This is due mostly to the large reduction in limestone's UEV. Nuclear energy is a minor (about 1% contribution) to the non-renewable metabolism of the US. The Proposition 1 (updated NEAD values plus nuclear energy of Uranium plus new biogenic limestone UEV) and the chemical exergy transformities method (Proposition 3) are the only two methods in which the energy of minerals (less limestone) appear notably on the scale of national energy accounting.

Wrapping it Together

To express the different effects of different forms of exergy Odum (1996) introduced a method of environmental accounting called emergy. In the emergy method transformities express exergy quality from the donor-perspective, that is the environmental exergy previously invested to yield a presently available exergy. However, mass is more convenient to account crustal minerals, thus specific emergy was defined to be the product of transformity and exergy density (J/g). In this way “mass quality” is characterized as the environmental effort in producing available potential energy in mass form.

We dispel summing chemical and concentration exergies, a common practice in the field of exergoecology, due to different reference datum (similar to the difference between thermal and kinetic exergy).

Negative chemical exergies make questionable the chosen reference environment used to calculate them. The chosen reference environment for this study produced the least number of chemical species with negative chemical exergies and has a chemical composition very similar to the present day crust. To use chemical exergies in our formulations we take their absolute value (because we cannot make use of negative mineral transformities).

There's only two previous attempts to link specific emergy and transformity for crustal minerals of varying purity (Jamali-Zghal et al., 2014; De Vilbiss, 2013). The work here parallels these initial efforts and goes deeper. For example, rather than defining the transformity of crust as the weighted average transformity of Earth's exergy sources (Jamali-Zghal et al., 2014), here it has been shown that the crust can be considered to have an average chemical exergy transformity based on crustal mass multiplied by

crustal age divided by the total chemical exergy of the crust. Also minerals can be modeled to possess unique transformities based on the ratio of average crustal specific energy to either their Gibb's mixing energy or chemical exergies.

The biogenic UEV of calcite was found from a reevaluation of a coral reef system (McClanahan 1990). Limestone was the biggest energy contributor the US in 2008. It's new UEV (1.66 E9 sej/g) is 17% of the original value.

For the first time ever we provide the energy contribution from nuclear resources to an economy. Using the Uranium transformity from Chapter 2 and NEAD data, the energy in 2008 of US Uranium mining was 1.06 E23 sej/yr. This value is however an overestimation as a more detailed understanding of the final fussion waste products should be undertaken. Here we simply assumed the final stable decay product from the ^{238}U decay chain (^{206}Pb).

Six methods were considered in this Chapter to compute the specific emergies of crustal minerals other than limestone. Of these six methods three were immediately dismissed for illogical premises. Of the remaining three just two, average crustal chemical exergy transformities and Gibb's transformities accounting mixing exergy, yielded the presupposed negative correlation between specific energy and mineral abundance. Minerals that are more abundant are presupposed to possess lower specific emergies. The methods which satisfy this are Gibb's transformities accounting only mixing exergy ($R^2 = 0.45$) and crustal average chemical transformity accounting total exergy ($R^2 = 0.20$).

To recommend a method we have four propositions. All propositions include updated the average crustal specific energy value from 1.68 to 1.38 E9 sej/g, the

nuclear energy of Uranium, and the new biogenic UEV for limestone. Proposition 1 is the updated NEAD values. Propositions 2, 3, and 4 utilize the methods of this paper to update the energy values for all the other crustal minerals besides limestone. These are crustal average chemical exergy transformity accounting total exergy (Proposition 2), chemical exergy transformities accounting total exergy (Proposition 3), and Gibb's transformities accounting only mixing exergy (Proposition 4).

Only Propositions 1 and 3 yield energy characterizations of the minerals which are of notable magnitude on the national scale. However, Proposition 1 provides no link between transformity and specific energy which is absurd because specific energy and transformity are always linked through specific exergy. Proposition 4 accounts only the mixing exergy using mineral transformities derived from Gibb's formation energies, which is exactly the way that fresh water is accounted in the energy method.

Proposition 1 is merely an update of the old mass enrichment method and highly non-recommended because of this. Propositions 2-4 make use of transformities which are fixed as mineral concentration changes. This is undesirable and is merely a phenomenon of our formulation of mineral transformity. Crustal average chemical exergy transformity (Proposition 2) also fixes transformity across all minerals (hence crustal average transformity) which is even less desirable than Propositions 3 and 4.

In the Gibb's and chemical exergy transformity methods the transformities of each mineral is held constant while specific exergy (and thus specific energy) change with purity. In these methods each mineral has a unique transformity and specific energy (when above average; at average concentration they have unique transformities but the same average crustal specific energy value).

There may be a better method yet to discover, however this is absolutely the best yet when it comes to underscoring the emergy of crustal minerals with a thermodynamic formulation and methodologically consistent principles congruent with the overall emergy method.

Using Proposition 4, our recommended Proposition, the following are results of this study compared with the 2008 US emergy metabolism as reported in NEAD. Limestone emergy is reduced to $1.6 \text{ E}24 \text{ sej/yr}$ (17% its original value). Nuclear emergy is now present with $1.06 \text{ E}23 \text{ sej/yr}$ contribution (0.4% total). The emergy of other minerals/metals is reduced to $9.1 \text{ E}21 \text{ sej/yr}$, or about 4.58% the original NEAD value. Concentrated non-renewables are now reduced to $11.3 \text{ E}24 \text{ sej/yr}$ (about 57% the NEAD value). The overall US empower of the 2008 economy is reduced from 35.9 to $27.44 \text{ E}24 \text{ sej/yr}$, a 23% reduction. Now the US is only utilizing 2x the renewable empower of the entire Earth rather than 3x the GEB, simply by modifying some accounting methods.

Table 4-1. Most important metal and mineral energy inputs in 2008 to the US economy (data from NEAD, 2014)

Item	Mass (2008 MT)	Specific energy (sej/g)	Energy (2008 E22 sej)	% tot	Type	Mass enrichment or source ¹	Mean crustal abundance mg/kg	Mine crustal abundance mg/kg
Limestone	885203000	9.50 E09	841	83%	Mineral	Limestone		
Dolomite ²	59400000	9.50 E09	56	6%	Mineral	Limestone		
Iron ore	54000000	5.78 E09	31	3%	Metal	3.4	56300	193780
Lead	423000	4.80 E11	20	2%	Metal	285.7	14	4000
Phosphate rock	30900000	6.45 E09	20	2%	Mineral	3.8	1050	3990
Copper	1310000	9.80 E10	13	1%	Metal	58.3	60	3500
Gypsum ²	12700000	9.50 E09	12	1%	Mineral	Limestone		
Zinc	778100	7.20 E10	6	1%	Metal	42.9	70	3000
Molybdenum	61400	7.00 E11	4	0.4%	Metal	416.7	1.2	500
Cadmium	745	3.36 E13	3	0.2%	Mineral	20000.0	0.15	3000

¹ Mass enrichment means the ratio of mine grade to average crustal abundance. ² The UEV of dolomite and gypsum was approximated to that of limestone in NEAD.

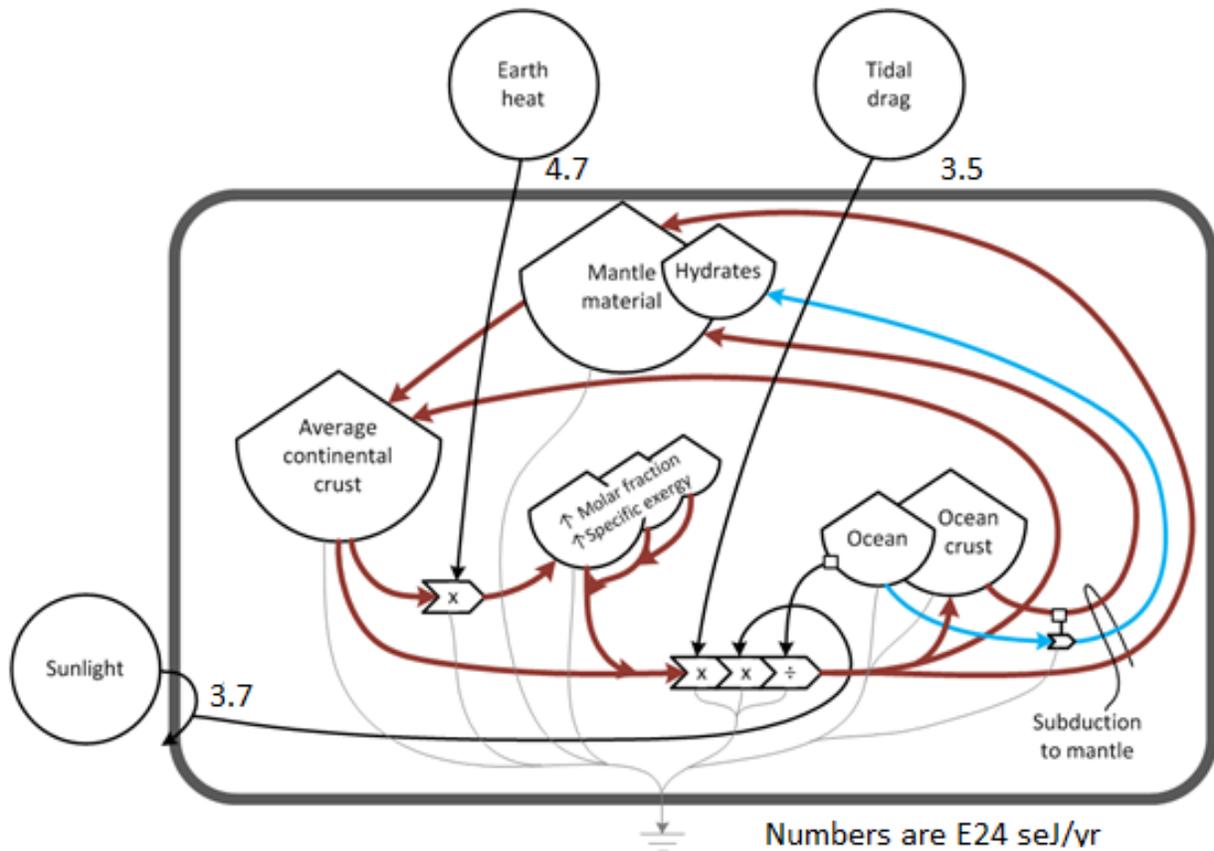


Figure 4-1. Systems diagram of continental cycling, showing the GEB driving the mineral cycles of concentration and crustal accretion (numbers from Brown et al., 2016).

Table 4-2. Selected minerals with negative chemical exergies (from Valero et al., 2012)

Commonly extracted Minerals	Formula	Chemical exergy (J/g)	Average crustal abundance (parts per billion)
Colemanite	$\text{Ca}_2\text{B}_6\text{O}_{11}(\text{H}_2\text{O})_5$	-1938	0.38
Orthoclase/K-feldspar	KAlSi_3O_8	-46	2,676
Apatite	$\text{Ca}_5(\text{PO}_4)_3(\text{OH})_{0.33}\text{F}_{0.33}\text{Cl}_{0.33}$	-46	5.02
Kaolinite	$\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$	-35	206
Diaspore	$\text{AlO}(\text{OH})$	-22	187
Hydragillite/Gibbsite	$\text{Al}(\text{OH})_3$	-18	112

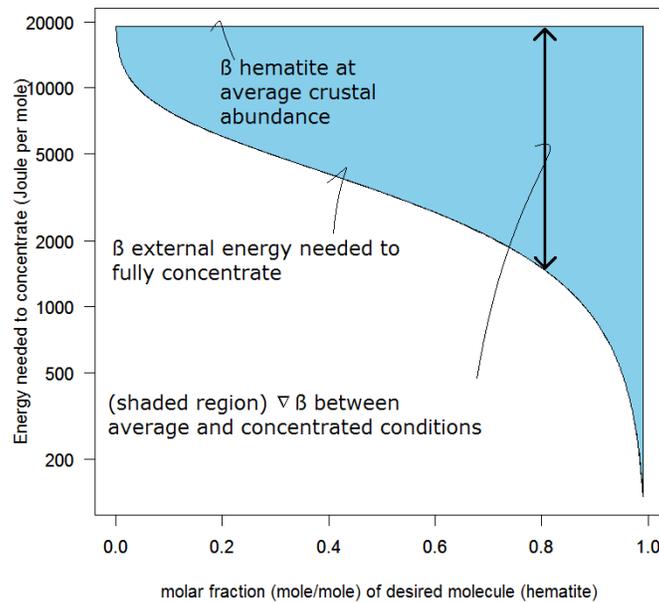


Figure 4-2. (top-horizontal line) energy needed to concentrate to purity from average crustal abundance, (bottom curve) concentration energy with variable concentration, and the difference (shaded region) which represents the potential (concentration exergy) for the mineral hematite.

Table 4-3. Unique mineral chemical and Gibb's transformities for the 10 most important minerals for the US economy ¹

Item	Mineral <i>i</i>	Mine abundance (mg/kg) ²	Molar mass (g/mol)	Average molar fraction, \bar{x}_i	Mine molar fraction, $x_{i,mine}$	Mixing exergy (J/g)	$\bar{\tau}_{\Delta G,i}$ ³ (sej/J)	$\bar{\tau}_{ch,i}$ ³ (sej/J)
Limestone	Calcite	950000	100.09	1.26 E-02	9.68 E-01	107.5	1.21 E7	8.60 E9
Dolomite	Dolomite	950000	184.4	1.20 E-03	9.42 E-01	89.6	3.43 E6	1.03 E9
Iron ore	Taconite	193780	215.6	2.87 E-05	1.50 E-01	98.4	7.16 E6	1.24 E9
Lead	Galena	4000	239.3	4.40 E-06	2.64 E-03	66.3	4.61 E7	1.94 E6
Phosphate rock	Phosphate rock	3990	310.2	1.42 E-03	2.05 E-03	3.0	1.14 E6	8.56 E7
Copper	Chalcopyrite	3500	183.5	5.71 E-05	3.01 E-03	53.6	3.45 E7	9.18 E5
Gypsum	Gypsum	950000	762.1	1.26 E-04	7.97 E-01	28.5	9.96 E5	2.44 E8
Zinc	Sphalerite	3000	97.5	1.61 E-04	4.85 E-03	86.6	6.38 E7	1.91 E6
Molybdenum	Molybdenite	500	160.1	1.80 E-06	4.93 E-04	86.9	2.93 E7	8.38 E5
Cadmium	Greenockite	3000	144.5	1.26 E-07	3.27 E-03	174.4	4.92 E7	1.96 E6

¹ Data from Valero et al. (2012) except for ² from NEAD (2012); ³ Using eq. 4-1 and 4-2 in text. *Note the transformities for calcite, dolomite, and gypsum are not used later and rather the biogenic UEV for calcite is used.

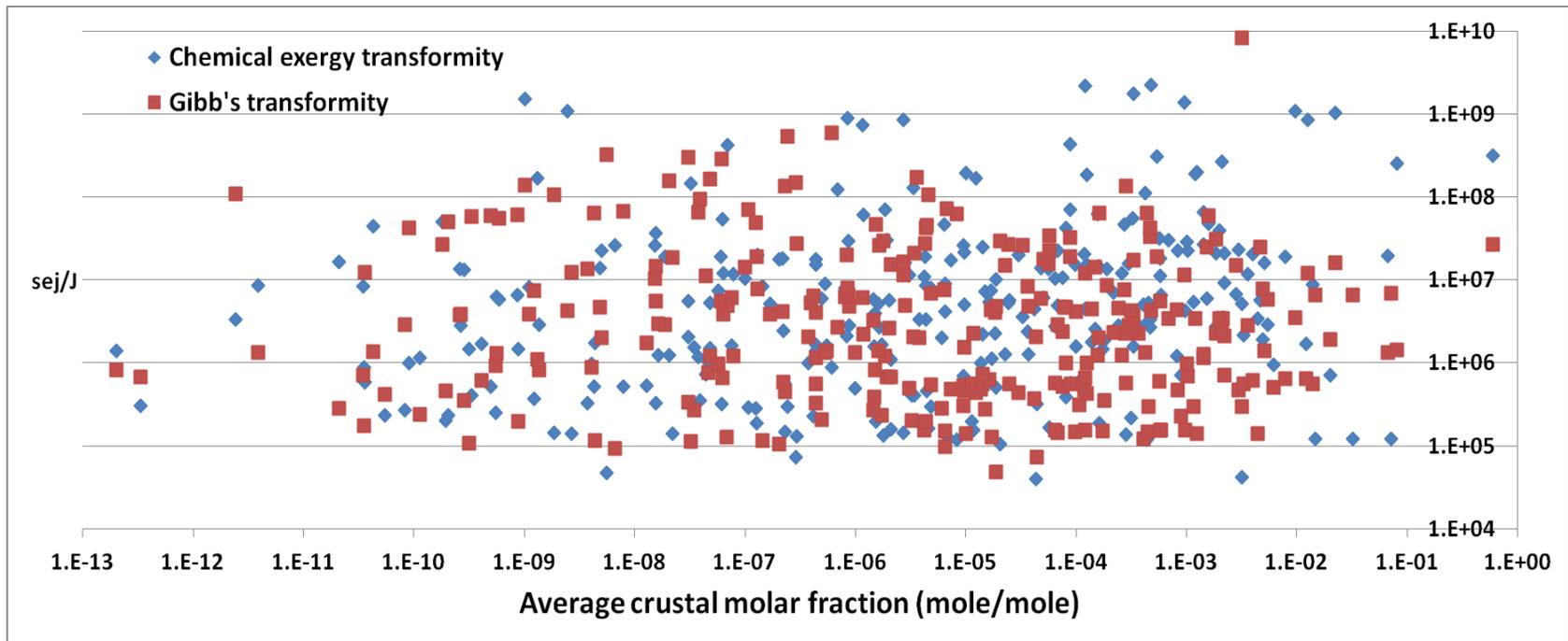


Figure 4-3. The 281 crust minerals for which Gibb's formation energy and chemical exergies are found (data from Valero et al., 2012). No correlation between average crustal abundance and transformity, although Gibb's transformities are generally smaller.

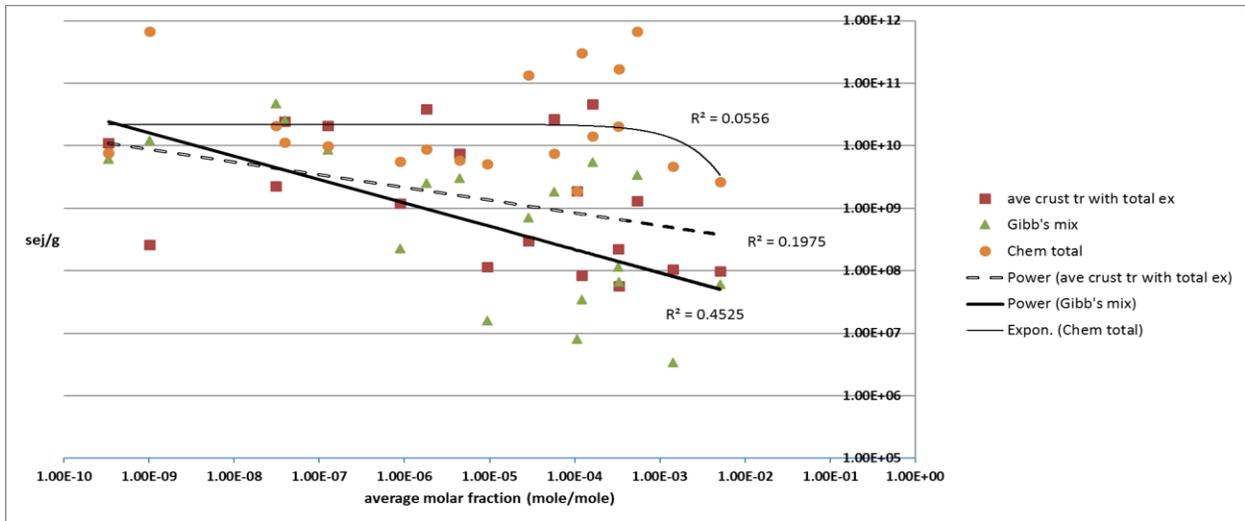


Figure 4-4. Specific emergy (y-axis) vs. molar fraction at average abundance of 20 minerals accounted in the NEAD which we have transformities and thus specific energies for.

Table 4-4. Specific emergies (E9 sej/g) of important mineral inputs to the 2008 US economy when applying two different transformities (Gibb's and chemical exergy) with two accounting procedures (total energy or mixing exergy only).

Item	2008 US consumption (MT)	NEAD updated ¹	using $\tau_{\Delta G}$ mixing J ²	using τ_{ch} Total J ³	using $\bar{\tau}_{crust}$ Total J ⁴
Limestone	885,203,000	7.8	1.7	1.7	1.7
Dolomite	59,400,000	7.8	1.7	1.7	1.7
Iron ore	54,000,000	4.7	0.7	133.3	3.0
Lead	423,000	392.0	3.1	5.9	75.7
Phosphate rock	30,900,000	5.3	0.0034	4.7	1.1
Copper, mine	1,310,000	80.0	1.8	7.6	267.6
Gypsum	12,700,000	7.8	1.7	1.7	1.7
Zinc	778,100	58.8	5.5	14.3	458.0
Molybdenum	61,400	571.6	2.5	8.7	385.9
Cadmium	745	27,400.0	8.6	9.9	207.8
TOTAL (E24 sej/yr) ⁵		8.2	1.6	9.0	2.6
% limestone ⁶		90%	97.17%	18%	62%
% original NEAD ⁷		82%	16%	89%	25%

¹ NEAD (2012) specific emergies are updated to the new average crustal specific emergy (1.38 E9 sej/g) from the old (1.69 E9 sej/g used in NEAD); ² Eq. 4-9; ³ Eq. 4-7; ⁴ Eq. 4-10; ⁵ The product of each column with the 2008 US consumption column (note 1 E6 g per metric ton; MT). ⁶ The sum of total emergy from limestone, dolomite, and gypsum (all of which possess the limestone UEV) divided by total emergy for that method. ⁷ Original NEAD value for total 2008 US mineral/metal consumption is 10.1 E24 sej/yr.

Table 4-5. Proposed mineral transformity methods which were analyzed for the presupposed negative relationship between abundance and mineral specific emergy.

	Gibb's transformity	Chemical exergy transformity	Crustal average chemical transformity
Account only mixing exergy	(Eq. 4-9)		
Account total exergy		(Eq. 4-7)	(Eq. 4-10)

Table 4-6. Emergy evaluation of limestone precipitating coral reef system. Data from McClanahan (1990), updated with new transformities here

Item	McClanahan (1990) J/m2/yr	Updated J/m2/yr	McClanahan (1990) sej/m2/yr	Updated sej/m2/yr
Sunlight	7.10 E9	7.10 E 9	7.10 E 9	7.10 E 9
Waves	9.93 E 8	4.45 E 8	8.23 E 12	3.69 E 12
Tides	1.07 E 8	1.8 E 7	7.75 E 12	1.3 E 12
Currents	6.62 E 8	3.65 E 6	6.39 E 13	3.52 E 11
Rain chemical ¹	5.01 E 6	5.01 E 6	3.30 E 10	3.30 E 10
Rain kinetic ²	3.08 E 4	2.08 E 6	3.75 E 8	2.54 E 10
Wind	-	-	-	-
Deep heat ³	-	2.71 E 6	-	5.50 E 10
Total (sej/m2/yr)			6.39 E 13	3.69 E 12

¹ Calculated chemical exergy of rain using McClanahan's rainfall data, but he doesn't account rain chemical exergy.

² McClanahan uses terminal rainfall velocity to calculate rain KE then uses the transformity for terrestrial stream geopotential to estimate the emergy of rain KE. I also use this transformity (as I have nothing better, however, likely the geopotential transformity of vapor in clouds would be even smaller) but estimate the geopotential dissipated in rainfall by assuming rain occurs from a 200m height.

³ I estimate here deep heat as 86 mW/m2. McClanahan doesn't account deep heat.

Table 4-7. E9 sej/g limestone according to different areal empower intensities (from Table 4-5)

Calcite deposition rate (kg/m2/yr)	McClanahan (1990)	Current updated	Odum (1996) ¹
2.221 ²	28.8	1.66	19.6

¹ Geologic rather than biologic production process.

² McClanahan (1990)

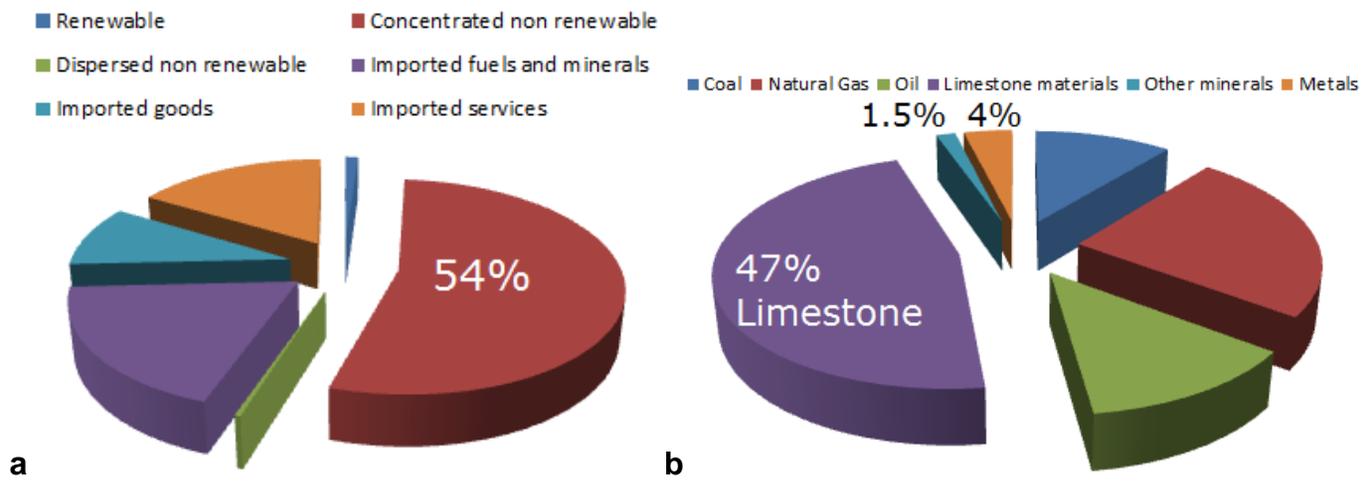


Figure 4-5. Energy contributions to the US economy from a) all resources; b) breakdown of concentrated non-renewables (data from NEAD).

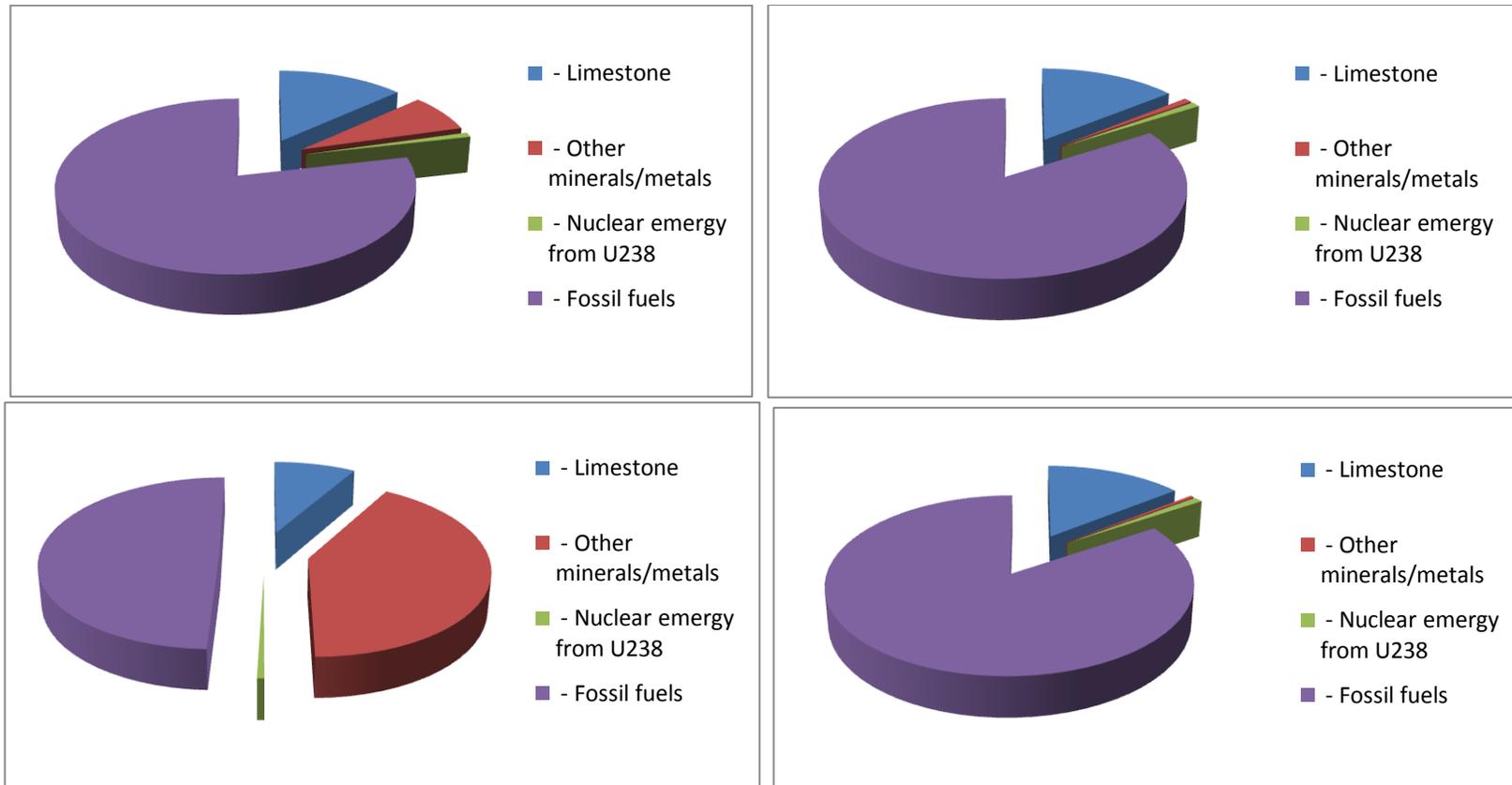


Figure 4-6. Total concentrated non-renewable energy accounted in the 2008 US economy. Fossil fuels, nuclear energy, and limestone are held constant, with limestone accounted using the new biogenic UEV. Other minerals/metals are accounted using (top-left) updated NEAD values to new average crustal specific energy, (top-right) crustal average chemical exergy transformity accounting total exergy, (bottom left) chemical exergy transformities accounting total exergy, and (bottom-right) Gibb's transformities accounting only mixing exergy.

CHAPTER 5 CONCLUSIONS

In this dissertation I have presented the computations for updating several old energy characterizations, as well as produced many new energy characterizations (specific energies and transformities). There are several contributions which will greatly affect all energy research studies from now on. These include radionuclide transformities, a new geo-biosphere energy baseline, and updated UEVs for all the crustal minerals. A summary of the nuances in these discoveries are presented in this Chapter.

Radio nuclides are valuable for their nuclear exergy in addition to their energy of heightened concentrations in Earth's crust. Unlike other mineral bodies which can be totally evaluated in the energy method based on their crustal abundance, radionuclides require an additional form of measure which accounts their nuclear exergy. To tackle this issue, we perform an energy analysis of the stellar nucleosynthesis process which formed the heavy radioisotopes that contribute to Earth's deep heat and to human economies. Then as a rough estimate of the nuclear energy contributed through nuclear fission (nuclear power) we assume the total exergy of ^{238}U is used for the total of annual uranium extraction. This is an overestimate, as some exergy remains after the fission reaction which is why the waste isotopes are buried in the earth. However, this first approximation is a never before seen quantity in any energy accounting scheme.

The gravitational potential energy (GPE) required for the stellar nucleosynthesis represents the energy to compute the gravitational transformity of sunlight and heavier radionuclides. By assuming gravity is the same everywhere, we draw an equivalence between the transformity of sunlight and that of radionuclides. This solar equivalence

ratio (SER) is the basis for comparing and aggregating the sources of exergy to Earth into the GEB (geobiosphere energy baseline). We use thermal energy as a proxy for GPE generalizing that thermal energy is always precipitated by gravity, because increases in temperature require a concentration of particles, and gravity is the only effective force at this scale.

The general transformity of sunlight is the weighted gravitational transformity of the PPI and PPII fusion cycles ($7.65E-4$ gej/J). This value seems counterintuitive at first because a transformity below 1.0 suggests more energy is output than input (transformity is the inverse of efficiency). This is in fact what our quantity communicates, principally because we do not account the energy of the mass lost (termed mass defect) in nucleosynthesis. The reason we exclude mass defect is because the mass of atoms (neutrons and protons) is generated in processes outside of stars namely in big bang nucleosynthesis. We would need to assume some gravitational energy responsible for the initial cosmic production of these nucleons which is beyond our clear understanding. The future of gravitational energy, and the energy of stellar nucleosynthesis should focus on this area of knowledge.

Type II supernova conditions were modeled to calculate the energy of heavy radioisotopes ^{40}K , ^{232}Th , ^{235}U and ^{238}U , which are all the main radiogenic contributors to geothermal heat. The radioisotope energy is expressed in solar equivalent Joules so it may be aggregated with sunlight energy. A novelty of this approach is that solar equivalent Joules are not actually energy. The Sunlight did not produce radionuclides; they are both products of dissipated GPE. The gravitational exergy becomes the energy, and the light and heavier elements are co-produced in the stellar fusion

process. This brings into the discussion the description of the geo-biosphere energy baseline in which all the geo-biosphere's sources are independent of each other, and yet all were produced by gravitational exergy. They are all equated to each other using the gravitational transformity of sunlight discussed in Chapter 3.

The solar equivalent Joules of the main radionuclides of the Earth range from 3,650 seJ/J for ^{238}U to 8,050 seJ/J for ^{40}K . Counter intuitively the SER decreases as radionuclides get heavier. This is because the increase in radiogenic exergy (radiation output of the radionuclide in route to a stable isotope) of heavy isotopes increases faster than the accumulation of gravitational energy needed for their formation.

Chapter 2 contributes many new and unique concepts. First never before was there an energy characterization for nuclear exergy, either transformity or specific energy. Secondly, the fundamental equivalence between the independent sources of exergy to Earth are revealed through the use of gravitational exergy as the energy source to Earth's exergy inputs. Third, the issue of units in energy is resolved, where energy is expressed in emjoules (ej) and equivalent Joules (eJ) are used to communicate the units of the baseline and nowhere else.

Chapter 3 integrates the novelties of Chapter 2 and presents several novel energy approaches to underscore the complete geo-biosphere energy baseline. We develop further the idea that sources of energy to the geobiosphere are independent of each other, and that they're in no way transformations of sunlight. Solar equivalent exergy, and not solar transformity, must be used to describe the quality of deep earth heat and tides. The Earth exergy sources are aggregated into a single unit of measure (solar equivalent joules) which after all is the main utility of the energy method.

Two other novelties of Chapter 3 are 1) the separation of deep earth heat into relic heat and radiogenic heat, and 2) tides are understood as an outflow of Earth's rotational kinetic energy, which was itself induced by gravitational collapse during Earth's accretion. Moon and Sun despins the Earth in a process known as tidal drag. Ultimately all tides become dissipated heat or lunar orbital potential energy (a small portion goes toward increasing Earth's orbital potential around the Sun, but this was not evaluated). All of Earth's tides (there are land and atmospheric tides also) draw their energy from Earth's rotational kinetic energy.

Once a gravitational transformity is calculated for each of the four independent Earth energy sources (two were calculated in Chapter 2) they are equated to sunlight and then summed to give the composite solar equivalent energy driving the geobiosphere known as the GEB.

The gravitational binding energy of the Earth is used to underscore the energy of Earth's rotational KE and relic heat. Earth's original rotational KE is calculated using the conservation of momentum law and the assumption the Earth and Moon were once one body (giant impact theory).

The original thermal energy of the Earth is the sum of the current thermal energy plus the past heat flow over Earth's lifespan. The original relic heat and the original rotational KE were generated by Earth's original GPE (represented by Earth's binding energy). The difference between the sum of relic heat and rotational KE from the binding energy is the inefficiency of the planet forming process, i.e. the heat lost during accretion. This remainder can be allocated in several ways depending on whether we consider KE or relic heat to be the main product of planet formation. Since the decision

of which product is the main product is arbitrary and a human decision, we could take an average. However, we choose to allocate the dissipated heat of planet formation proportionally to both relic heat and KE according to the magnitude of each's original storage. This is what is called a split in the emergy method, and is equivalent to saying the process of forming Earth's relic heat and her rotational KE are equally efficient. The drawback of this approach is that the gravitational transformity of relic heat equals that of rotational KE. However, the other options offer worse drawbacks as discussed in Chapter 3 and summarized next.

By-product allocation would have us consider one of the accretion products to be equal in quality to the original GPE, which is false. Co-product allocation is cumbersome and inflates the final GEB. The resultant GEB from Chapter 3 will not be utilized in future studies due to the contemporaneous GEB evaluations by two other sets of authors who perform a backwards calculation of the GEB. The backwards calculation suffers from a qualitative perspective of Earth dynamics such as the biogeospheric relationship between sunlight and sedimentary cycles. The forwards calculation method considers the transformation of gravitational exergy into Earth's exergy sources. However backwards calculation methods are bolstered by present day data which is much more accurate, testable, and available than the highly uncertain data regarding Earth's original heat content, the temperatures of supernovae, the utilization of translational kinetic energy as a proxy for gravitational exergy, and the allocation procedure for splitting Earth's accretion energy among its products. For these reasons the GEB from Chapter 3 is merely used to compare with the backwards calculation methods. In fact, Chapter 3 GEB ($13.9 \text{ E}24 \text{ seJ/yr}$) closely approximates the other two

contemporaneous methods ($12.0 \text{ E}24 \text{ seJ/yr}$) which is encouraging for all the methods involved. For Chapter 3 the main area of future research should focus on this issue of just how efficient was the formation of relic heat vs. how efficient was the formation of Earth's rotational KE. Also perhaps other methods to compute the gravitational transformity of sunlight other than using translational kinetic energy as a proxy (e.g. the annual shrinkage of the Sun's volume) could be explored.

The SERs of the geo-biosphere inputs do not depend on the magnitude of their power as is the case with backwards calculation methods. In other words, other methods which evaluate the GEB consider the geo-biosphere inputs to be interdependent, and thus the resulting SERs (or transformities as they are named in those studies) are influenced by the magnitude of their fluxes. The method presented here is not effected by their magnitudes because all the sources have their equivalences calculated totally independent of each other, and so their SERs depend only on the magnitude of the upstream GPE assumed necessary to create them. This forward calculation technique, using GPE as the source to the GEB, yields SERs which are unaffected by updates to global energy flux data, which is an inevitability as science advances particularly for deep earth heat data. This is the main philosophical and pragmatic benefit of our forwards calculation procedure.

Chapter 4 evaluates the emergy of crustal minerals as well as the nuclear emergy of Uranium from Chapter 2. The emergy of the US economy is updated with these new crustal and Uranium emergy values. Chapter 4 begins by asserting that every resource in emergy accounting has both a transformity and specific emergy. This is not as evident for resources such as wind or sunlight. However, it is possible to

express light and kinetic energy on a mass basis and thus their transformities as specific energy. Crustal mineral methods have not before now had a provision to connect transformity with specific energy. Thus crustal mineral energy has had little relation to the thermodynamic basis which underpins the whole of the energy philosophy.

Average crustal transformity is the energy of the crust divided by the exergy of the crust. Average crustal specific energy is the GEB multiplied by the average age of the continental crust and then divided by the mass of the continental crust. We use continental crust because this is where mineral mining occurs, the continental crust is much larger and older than ocean crust, and because its composition is more readily understood. Average crust is not mined for any use.

During the time of crustal genesis (the last 2.5 billion years) many of Earth's energy sources have varied. Sunlight, tides, and deep earth heat are all different in magnitude now than in the past, however this variable is not accounted in average crustal energy and is a source for future research.

Chapter 4 uses the reference environment (RE) from which chemical exergy is derived. The crust is considered an ideal mixture. Certain mineral species are 'chosen' as reference substances for others to have chemical exergy relative to. No matter which minerals are chosen, some of the mineral species in the data set of crustal minerals will possess negative chemical exergies, whereas all the rest will be positive. The meaning and interpretation of this as well as how to utilize negative chemical exergies remains unknown. The result of chemical exergies on both sides of zero is undesirable, albeit inevitable, and leads to a questioning of the nature of RE for the crust. However, the RE

chosen for this study from Valero et al. (2012) possesses the least species of minerals with negative exergies and also represents well the present day composition of the crust, two characteristics not held by other studies of crustal chemical exergy.

We use the absolute value of chemical exergy to formulate chemical exergy transformities because energy cannot make use of negative transformities.

Transformity is on an absolute scale. Part of the formula for chemical exergy (and also for Gibb's free energies) is a mixing term called mixing exergy. Mixing exergy is the difference in Gibb's free energy between the mine and the average abundance conditions. Accounting only mixing exergy, and not total free energy, correlates with how rain is accounted in the emergy method.

Mass is more convenient to account crustal minerals, however we must link thermodynamics to mass to maintain the basic premises of the emergy method (Odum, 1996). For this effort we formulate specific emergy as a function of specific exergy and transformity. These three indicators are inseparable when handling the emergy of crustal materials.

We dismiss summing chemical and concentration exergies due to difference in reference datum, a finding very important to the exergoecology discipline which commonly adds these together to indicate resource utility.

Gibb's free energy of each mineral is used to calculate Gibb's transformities unique for that mineral. Chemical exergy for each mineral is also utilized to create unique chemical exergy transformities for each mineral. The Gibb's transformities are nearly identical for all minerals. Chemical exergy transformities however range four orders of magnitude and give the highest UEVs to the most common minerals such as

calcite, and lowest to rarer minerals such as cadmium, explained further next. Utilizing the crustal average transformity yields reasonable specific emergies for all the minerals examined (i.e. rarer minerals have higher UEVs than more abundant minerals).

Limestone is the single largest contributing mineral emergy to the US economy, and so minor changes to its UEV have great implications downstream. According to NEAD in 2008, with the emergy characterizations used therein, 26% of US emergy comes from minerals/metals. Of this, 90% comes from limestone. In the previous methods which are used in NEAD, limestone (i.e. sedimentary rocks) are co-products of the same crustal cycle that generates the mineral ore deposits. The current method of this dissertation formulates all minerals to be splits and thus they are additive.

However, in the case of limestone which is primarily biologically generated rather than geologically a different method is used where emergy evaluation of a coral reef system yields the specific emergy of deposited calcite. This UEV for calcite represents the emergy of limestone, dolomite, and gypsum in NEAD and so we continue with this approximation. Thus the UEV of limestone, dolomite, and gypsum have the value from our reef analysis of $1.66 \text{ E}9 \text{ sej/g}$. All other mineral UEVs are computed with the three methods mentioned (Gibb's transformities accounting mixing exergy v. chemical exergy transformities accounting total exergy v. average crustal transformity account total exergy). Note we don't use total free energy for the Gibb's method because the energy of formation is what emergy is, we are only interested in the exergy content of minerals.

Of our three proposed methods the contribution from limestone (or minerals proxied by limestone) ranges from 18% (total exergy using chemical exergy transformities) to 97.17% (only mixing exergy using Gibb's transformities). Note that our

new average crustal specific energy (1.38 E9 sej/g) reduces the original NEAD value from mineral/metal energy from 10.1 E24 sej/yr to 8.22 E24 sej/yr. This value is not a reflection of any new method proposed, simply it is the result of updating the fundamental UEV for crust according with new scientific data. Of the three proposed methods, the total US mineral/metal energy ranges from 1.64 E24 sej/yr (mixing exergy with Gibb's transformities) to 8.96 E24 sej/yr (total chemical exergy with chemical exergy transformities).

We presuppose a negative relationship between specific energy and crustal abundance i.e. that rarer minerals possess higher specific energies and more abundant minerals. Only Gibb's transformities accounting only mixing exergy and the crustal average transformity accounting the total exergy yield this relation ($R^2 = 0.45$ and 0.20 respectively).

The final proposition of Chapter 4 is to 1) use the updated average crustal specific energy (1.38 E9 sej/g), 2) make use of the new limestone specific energy (an 83% reduction in limestone energy), 3) make use of the nuclear energy of Uranium, a contribution of 1.06 E23 sej/yr to the US economic metabolism, and 4) utilize the Gibb's mineral transformities accounting only mixing exergy. All these changes result in a 23% reduction of the 2008 US energy metabolism. The new energy of the US in 2008 is 27.4 E24 sej/yr, just two-times the GEB!

The novel innovations created and presented in this dissertation can be summarized as follows.

- Energy characterizations for the radionuclides (not available prior)
- Novel and more general formulation of the GEB including
 - a) the creation of gravitational transformities

- b) separation of relic deep earth heat from radiogenic heat
- c) the proper understanding of the mechanisms that generate Earth's tides.
- A thermodynamic connection between specific emergy and transformity of crustal minerals.
- The first ever emergy accounting of nuclear resource (e.g. the nuclear emergy of US consumed Uranium).
- The biogenic emergy evaluation of limestone.

All the above are powerful contributions to the rapidly growing and evolving discipline of emergy accounting. There are, of course, many ripe areas for future research into the subjects detailed in this dissertation. The novel findings presented here should help guide future research to unify emergy concepts and create a prosperous future for us all.

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BIOGRAPHICAL SKETCH

Christopher Daniel De Vilbiss graduated from Liberty High School in Eldersburg Maryland in June of 2004. He then went to the University of Oklahoma on a wrestling scholarship and subsequently earned his Bachelor of Science in industrial engineering in May 2009. Next he completed his Master of Science in industrial engineering under Dr. Hank Grant at the University of Oklahoma in May 2011. Chris relocated to Florida that autumn to commence studies under Dr. Mark T. Brown at the University of Florida in Gainesville, Fl. His research of energy and environmental accounting was published several times, and he completed two government manuscripts and presented at several conferences. Finally he earned his Ph.D. in environmental sciences in December of 2016.