Toward a more complete O_2 budget: The impact of processing metal oxides and sulfur

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Support from Bowdoin College

WAO4

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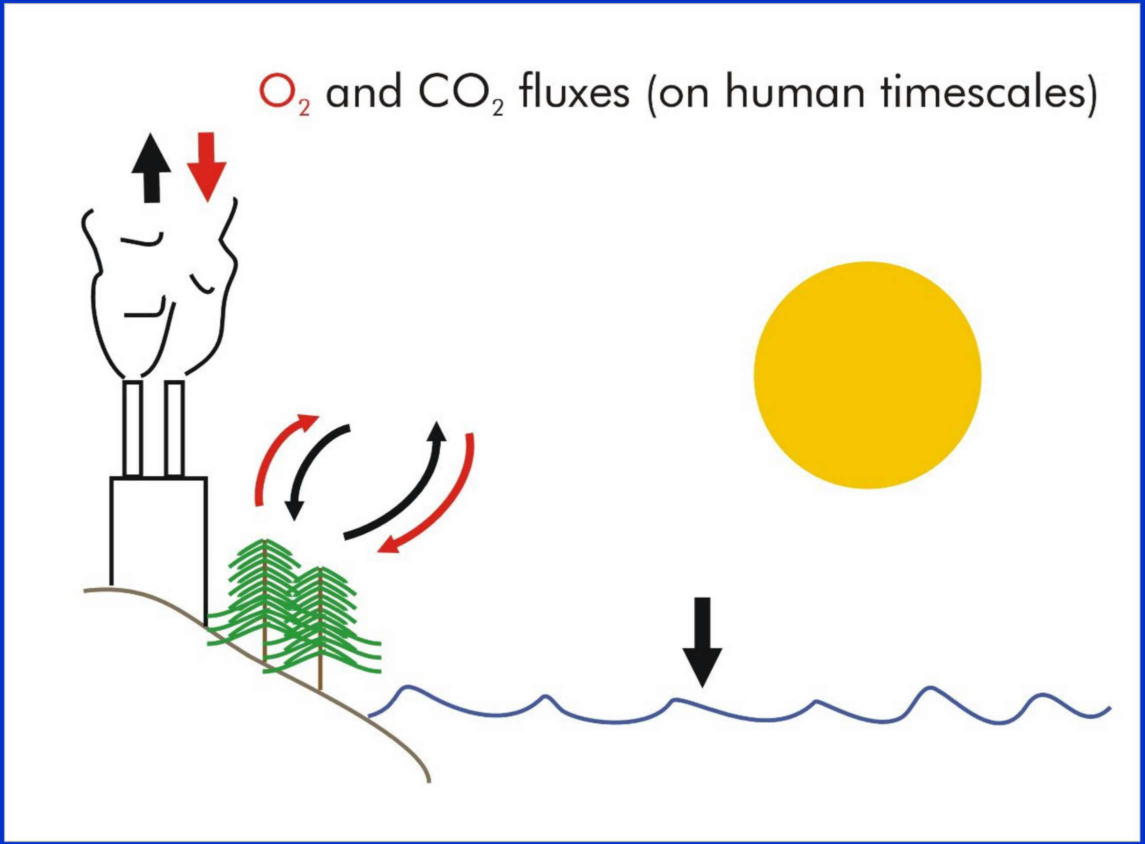
On the agenda:

- Motivation & overview
- Iron
- Aluminum
- Copper
- Sulfur
- Conclusions & next steps

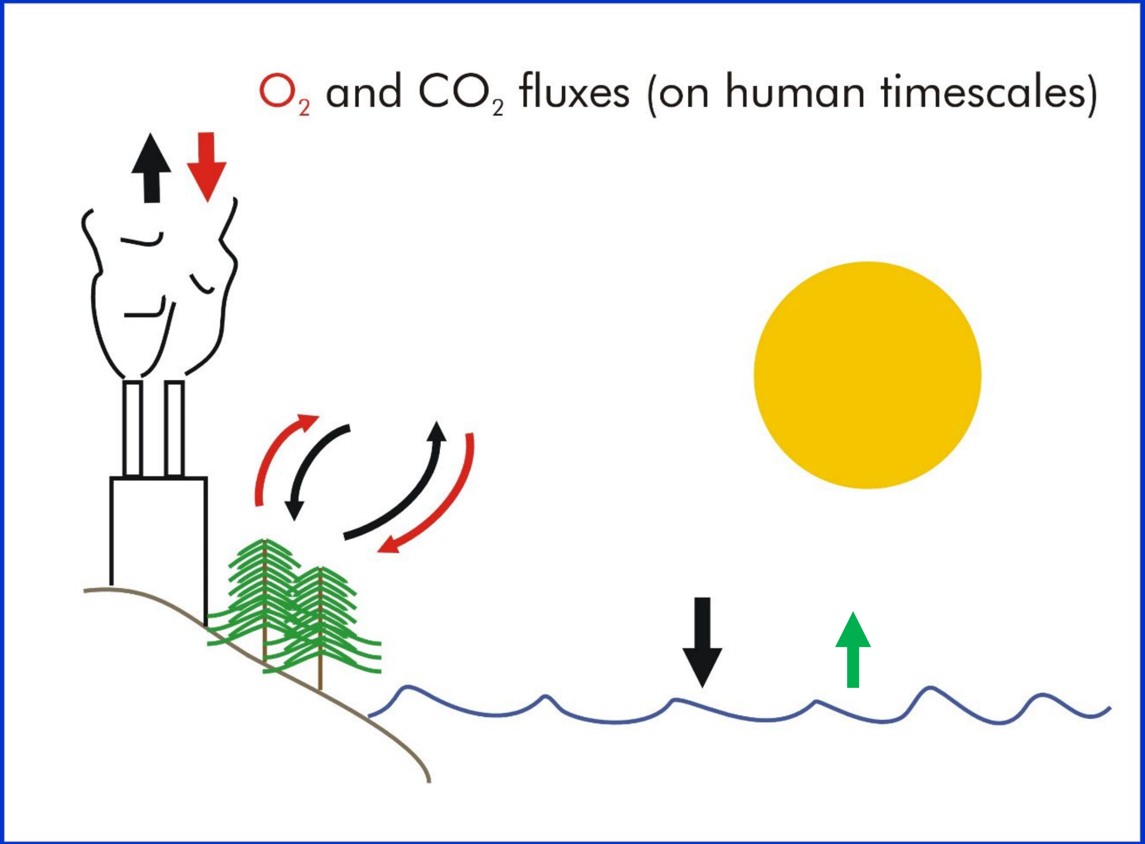
The canonical O_2 and CO_2 budgets



ΔCO_2 = Land biota + Industry + Ocean

ΔO_2 = Land biota + Industry

The updated O_2 and CO_2 budgets



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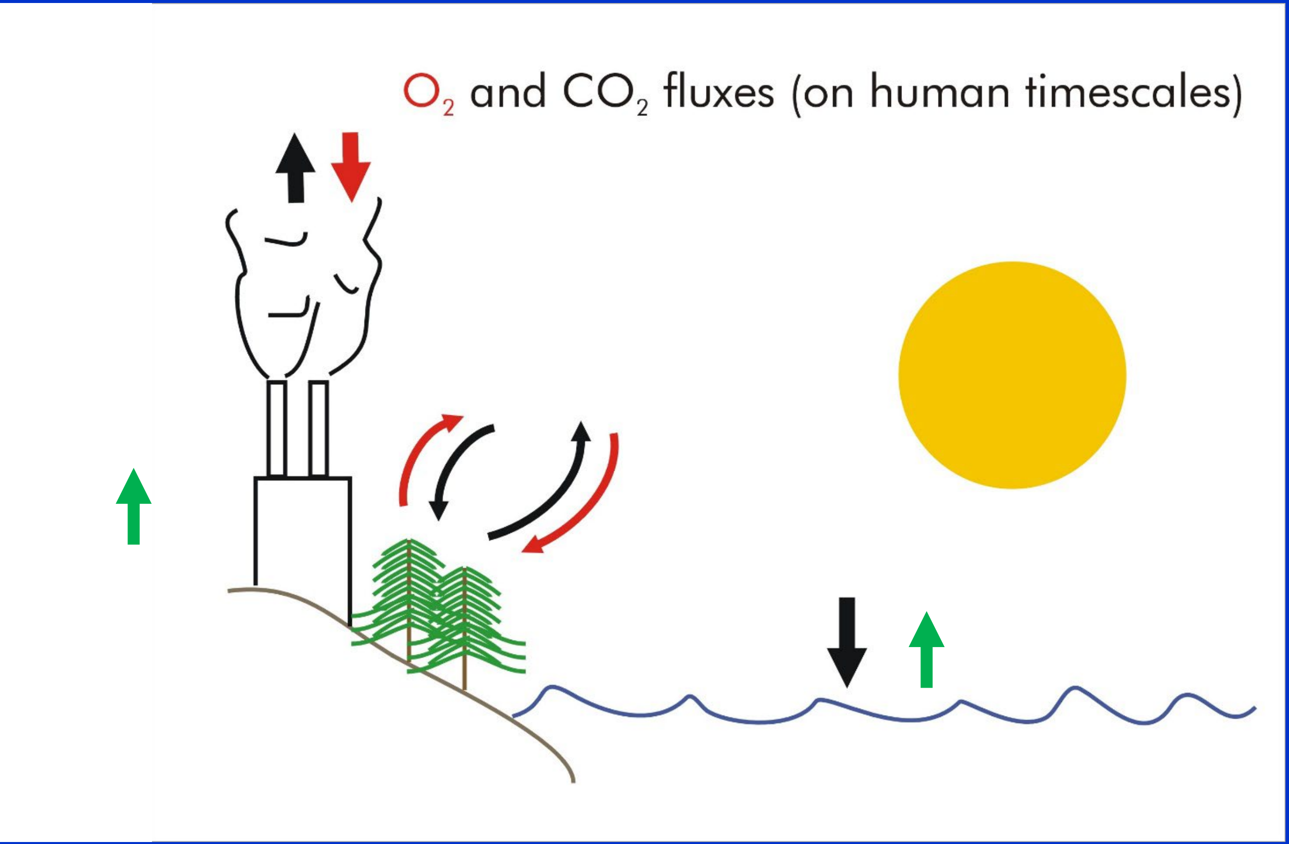
ΔO_2 = Land biota + Industry + Z_{ocean}

The upupdated O_2 and CO_2 budgets



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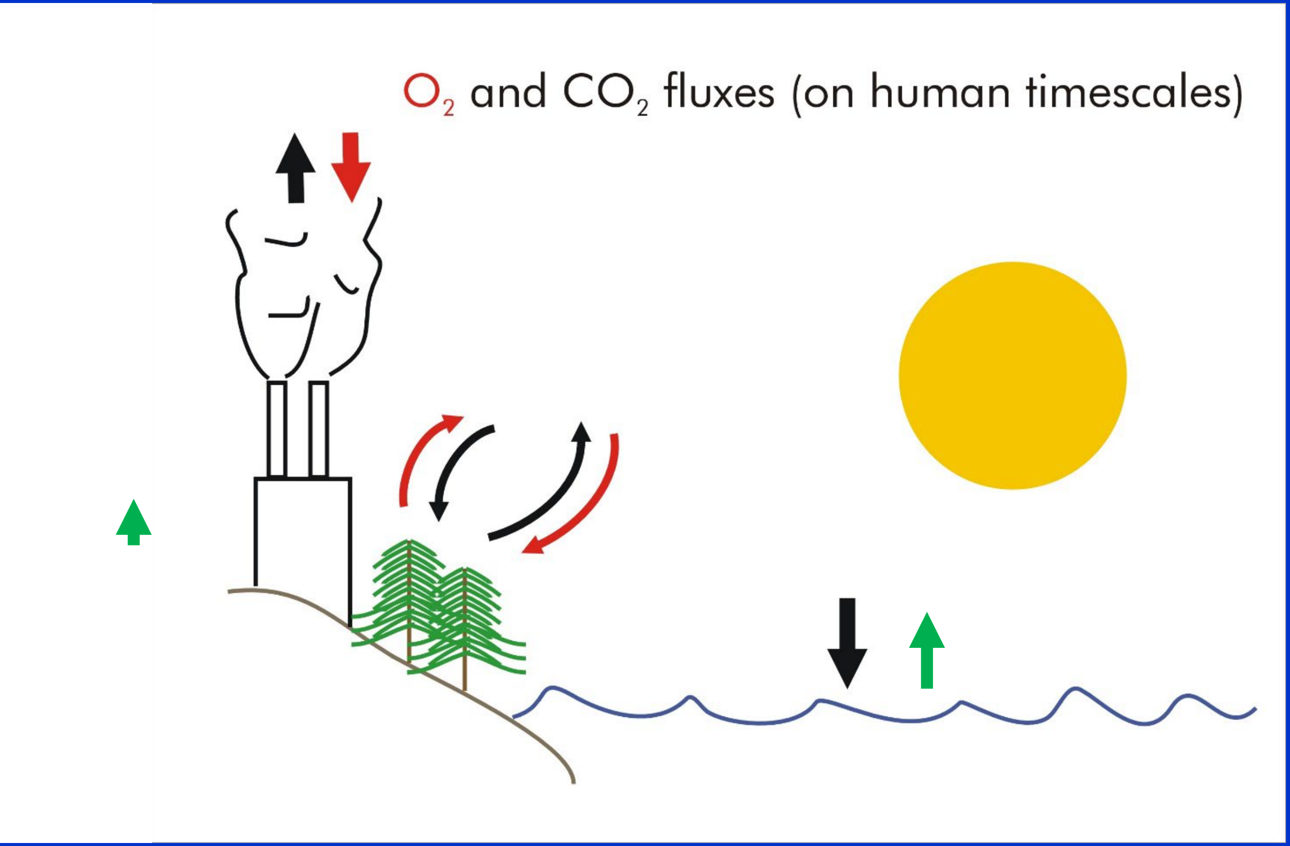

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Conceptual perspectives:

- Oxidized metals are being reduced, effectively yielding a flux of oxygen to the atmosphere
- The carbon in fossil fuels is being oxidized by something other than atmosphere

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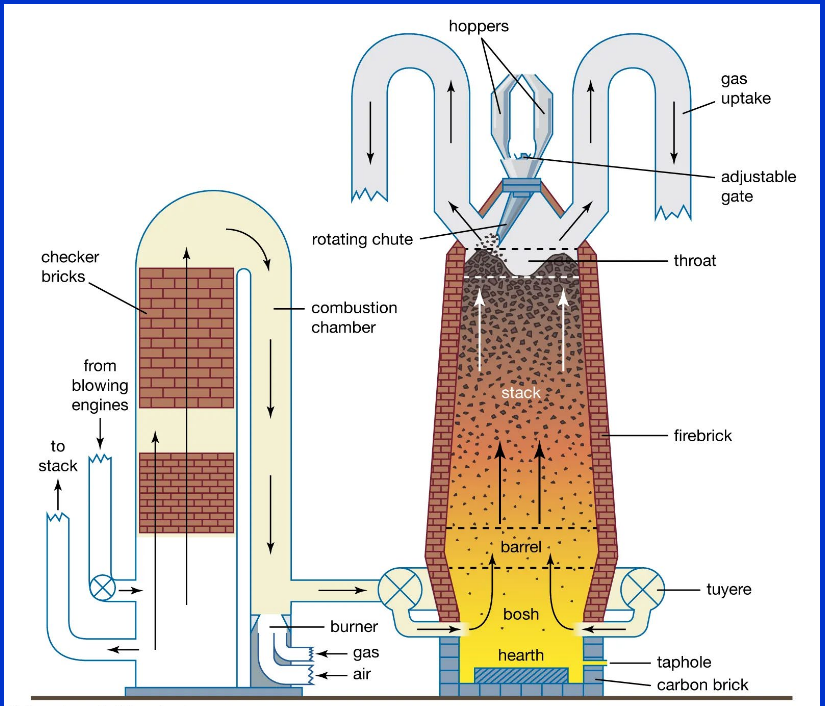
$$Z_{metals} = \Sigma\ production_i \times O_2\ yield_i$$

Iron, in detail

Iron oxides: 29 Tmol Fe in 2021 (USGS)

Fe_2O_3 and Fe_3O_4



Net reaction:

$$6C + 3O_2 + 2Fe_2O_3 \downarrow 4Fe + 6CO_2$$

https://www.britannica.com/technology/blast-furnace

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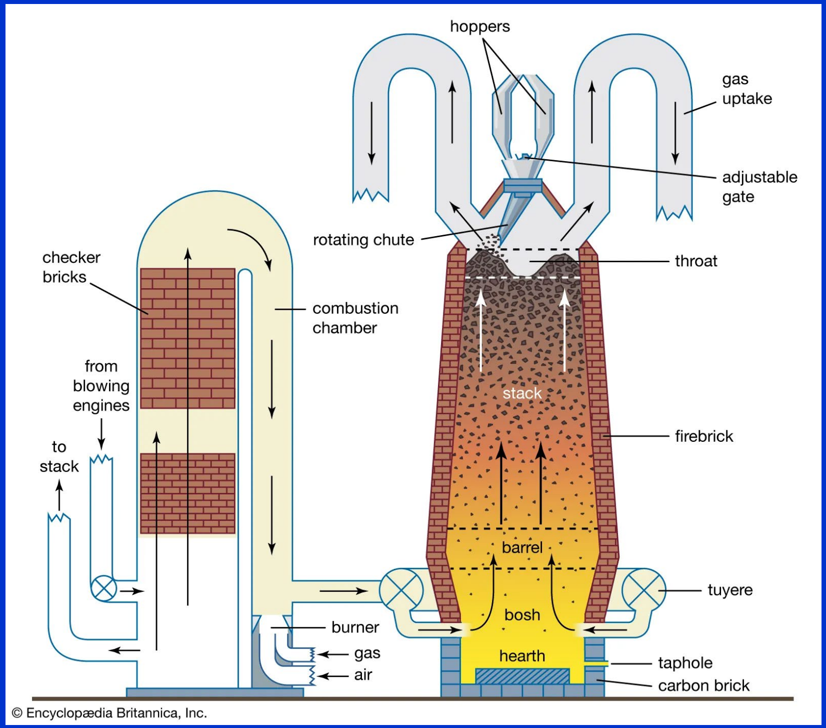

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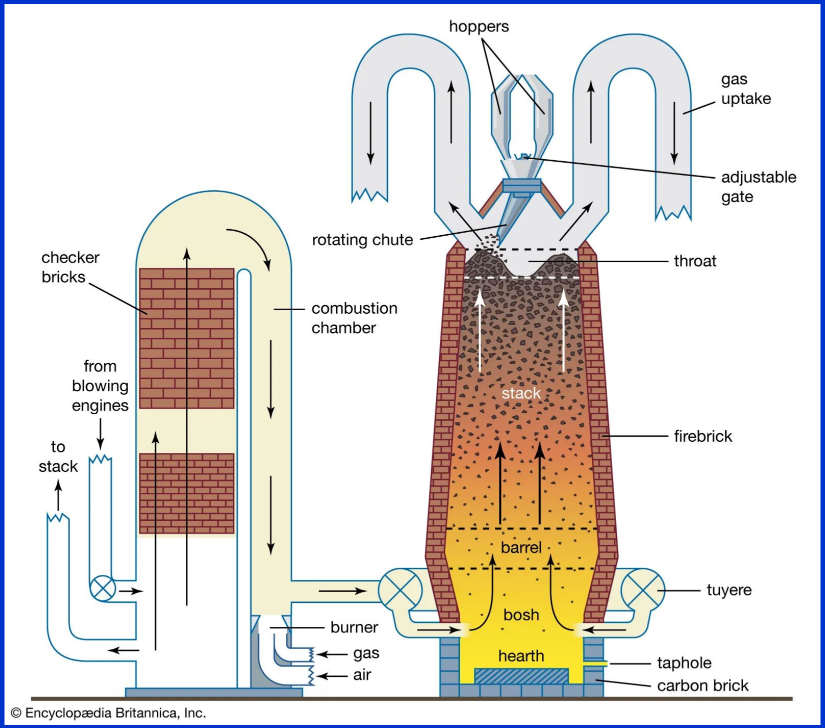

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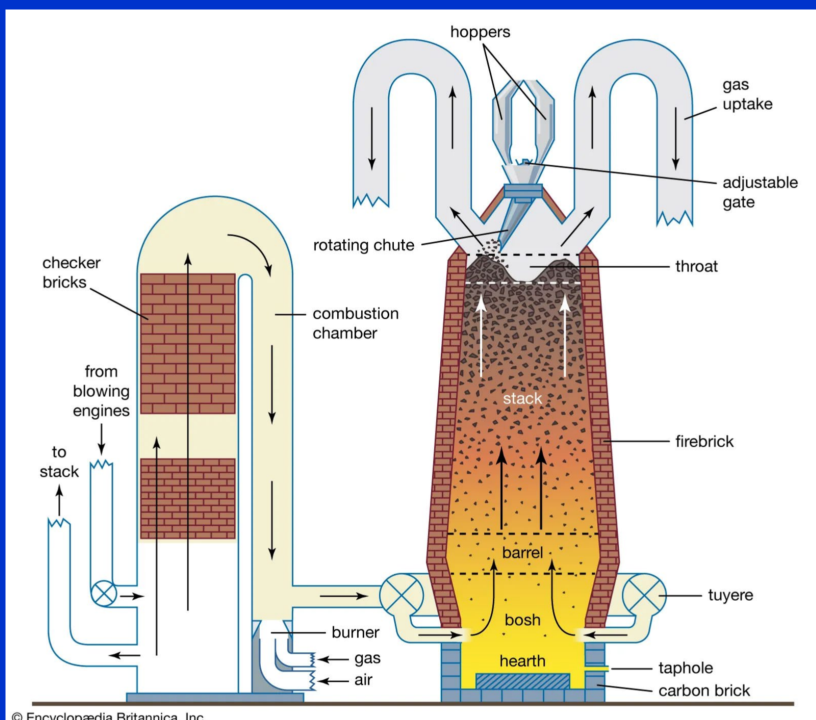

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Net reaction:

$$6C + 3O_2 + 2Fe_2O_3 \rightarrow 4Fe + 6CO_2$$

Net flux: 4moles Fe yields 3moles O_2

Hematite:

$$6C + 3O_2 + 2Fe_2O_3$$
$$\downarrow$$
$$4Fe + 6CO_2$$

Net flux: 4moles Fe yields 3moles O2

Magnetite:

$$4C + 2O_2 + Fe_3O_4$$
$$\downarrow$$
$$3Fe + 4CO_2$$

Net flux: 3moles Fe yields 2moles O_2

- Essentially all Fe is reduced*
- Hematite/Magnetite mixture not certain (80:20 is best guess*, but consider 95:5 and 50:50)
- Production uncertainties small (of order 0.75%)*

*Chris Tuck, USGS

Contributions to Z_{metals}

(snapshot in 2018)

Fe: 27.6 Tmol $\rightarrow$ +19.95 Tmol O_2

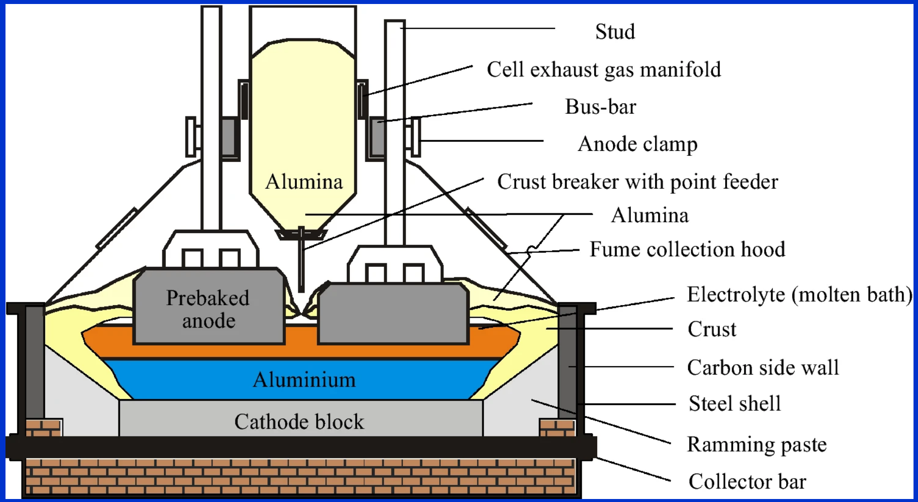
Aluminum in detail

Aluminum Oxides: 2.5 Tmol Al in 2021 (USGS)

$AlO(OH)$ $Al(OH)_3$

Bauxite → Alumina → Aluminum

$2Al_2O_3 \rightarrow 4Al + 3O_2$



https://link.springer.com/article/10.1007/s42452-019-0869-6/figures/1

Net flux:
4moles Al yields
3moles O_2

- 85% of bauxite goes to alumina. Balance is not reduced.*
- Reduction of bauxite liberates O_2 as water.
- All oxides yield same O_2 during refining to alumina
- 88% of alumina is fully reduced.*
- During reduction of alumina, carbon anodes release CO_2 with O_2 from the alumina.

*Lee Bray, USGS

Contributions to Z_{metals}

(snapshot in 2018)

Fe: 27.6 Tmol → +19.95 Tmol O_2

Al: 2.36 Tmol → +1.77 Tmol O_2

Copper in detail

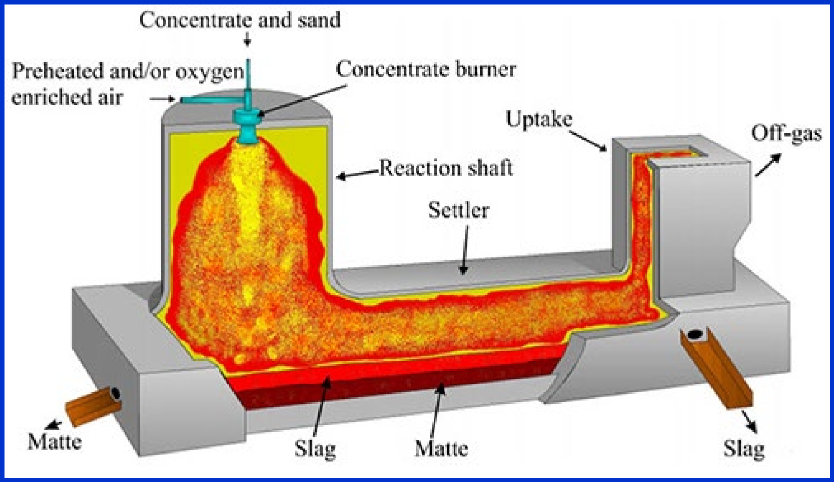
Copper oxides and sulfides: 0.33 Tmol Cu in 2021

(USGS)

Mostly sulfides, some oxides

Sulfides are O_2 sinks

$$CuFeS_2 \rightarrow \tfrac{1}{2}(FeO) + \tfrac{1}{4}(Fe_2O_3) + 2(SO_3)^*$$



Net flux:
1mole Cu
needs
3.625moles O_2

*Example: Chalcopyrite, not balanced

https://www.totalmateria.com/page.aspx?ID=CheckArticle&site=ktn&NM=394

- Recycled copper is irrelevant (no O_2 flux)
- Three different sulfide minerals and four oxides
- 85% of Cu production from sulfides*
- Sulfides liberate S and Fe, which oxidize with atm O_2 and H_2O
- Final states: H_2SO_4, FeO and Fe_2O_3
- Ignore oxides (complicated and limited in amount)

Chalcopyrite: $CuFeS_2$	Chalcocite: Cu_2S	Bornite: Cu_5FeS_4
Net flux: 8moles Cu sinks 29moles O_2	Net flux: 4moles Cu sinks 3moles O_2	Net flux: 40moles Cu sinks 53moles O_2

*Schlesinger et al. 2011

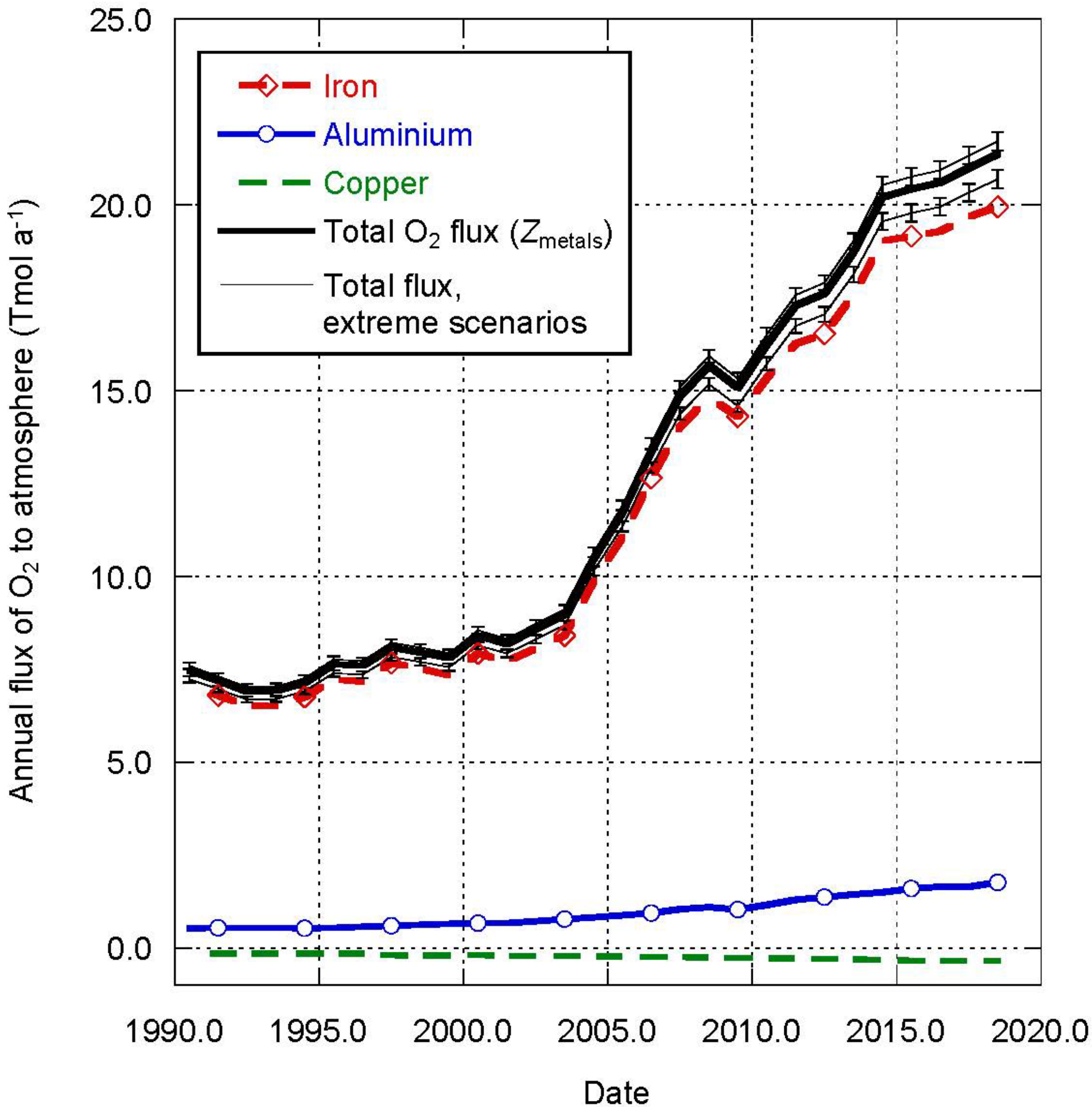
Contributions to Z_{metals}

(snapshot in 2018)

Fe: 27.6 Tmol → +19.95 Tmol O_2

Al: 2.36 Tmol → +1.77 Tmol O_2

Cu: 0.32 Tmol → -0.34 Tmol O_2



Iron
Aluminium
Copper
Total O2 flux (Zmetals)
Total flux,
extreme scenarios
Annual flux of O2 to atmosphere (Tmol a-1)
25.0
20.0
15.0
10.0
5.0
0.0
1990.0
1995.0
2000.0
2005.0
2010.0
2015.0
2020.0
Date

What does this mean for the oxygen budget?

(2000-2010)

$$Z_{metals} = 12.0 \,^{+0.2}_{-0.4} \text{ Tmol a}^{-1}$$

$$F_{ff} = 934 \pm 56$$

$$Z_{ocean} = 44 \pm 45$$

$$F_{land} = 96 \pm 77 \text{ (inferred)}$$

Keeling & Manning 2014

What does this mean for the carbon budget?

(2000-2010)

Without Z_{metals}

Ocean: 2.72 ± 0.6 PgC a^{-1}

Land: 1.05 ± 0.84

With Z_{metals}

Ocean: 2.86 ± 0.6

Land: 0.91 ± 0.84

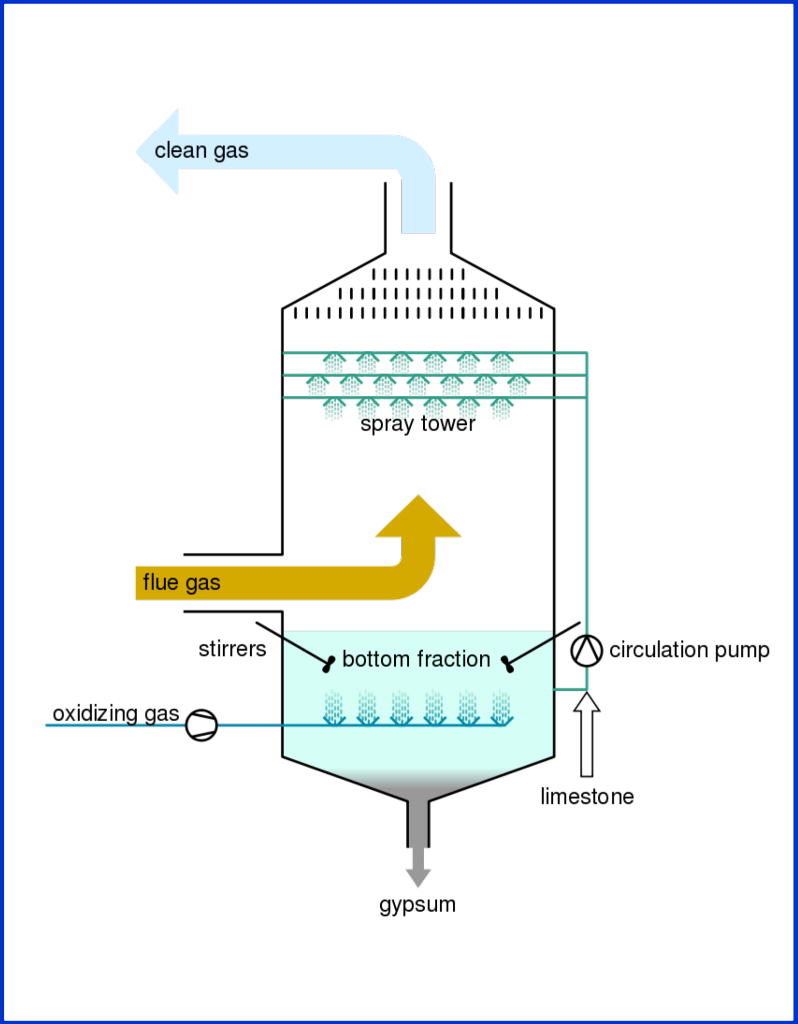
Keeling & Manning 2014

Looking ahead

- Z_{metals} evolves
- New methods of refining iron
- Move on from Bauxite
- More copper sulfides from deeper mines
- Will rusting of Fe catch up with production?

What about sulfur?

https://www.showcaves.com/english/explain/Resources/Sulfur.html



https://en.wikipedia.org/wiki/Flue-gas_desulfurization

- Transformed since the 1970s
- Currently 8% discretionary (mined), 92% non-discretionary (byproducts)
- Nearly all linked to FF production & combustion
- Starts in a reduced state – O_2 sink
- Built into α_{ff} (via C,H,S,N ratios in $\alpha_{gas,}$ $\alpha_{liquid,}$ α_{solid}) assuming H_2SO_4 final state

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The calculation of α_{ff}

(Keeling 1988, eq. 4.15)

$$CH_wO_xS_yN_z + (1 + w/4 - x/2 + 3y/2 + 5z/4)O_2$$
$$\downarrow$$
$$CO_2 + (w/2 - y - z/2)H_2O + yH_2SO_4 + zHNO_3$$

Oxidative ratio (α): coeff O_2/coeff CO_2

$$\alpha_{ff} = \Sigma c_i \alpha_i$$

where i = gas, liquid, solid

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Oxidative ratio (α): coeff O_2/coeff CO_2

$$\alpha_{ff} = \Sigma c_i \alpha_i$$

where i = gas, liquid, solid

- α_{gas} & α_{liquid} are fine
- α_{solid} not correct (flue gas desulfurization)

FGD: Add $CaCO_3$ or CaO, produce $CaSO_3$ or $CaSO_4$

Adjusting α_{ff} is complicated.

Estimate: ΔOcean carbon sink = -0.03Pg a^{-1}
ΔLand carbon sink = +0.03Pg a^{-1}

Overall Conclusions:

- Ignoring metals isn't a big deal
- Including metals increases estimated ocean uptake by ~0.14PgC a^{-1} (previously 2.27+/-0.60) and decreases land equivalently.
- Changes are small compared to uncertainties, but still important. Use Z_{metals}!
- Sulfur is more complicated, but also a much smaller influence.