

AQUEOUSLY ALTERED PLANETESIMALS OXIDIZE ROCKY PLANETS ACROSS THE GALAXY.

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Introduction: The oxygen fugacity (f_{O_2}) of the solar gas that comprised the solar protoplanetary disk was approximately 7 orders of magnitude lower than that defined by the iron-wüstite (IW) reference reaction. CAIs, enstatite chondrites, aubrites, and Mercury record these low solar-like values for f_{O_2} . The majority of rocks, however, represented by Earth, Venus, Mars, and most other meteorite groups, have intrinsic oxygen fugacities at least 10^5 greater than a gas of solar composition. There is considerable debate about the processes that led to this high oxidation state for the vast majority of Solar System rocks.

We recently found that extrasolar rocks accreted by white dwarf stars (WDs) have high f_{O_2} values resembling carbonaceous and ordinary chondrites [1]. Here we report more WD f_{O_2} values (Fig. 1), and consider the implications of the widespread occurrence of relatively oxidized rocks across the Galaxy. We conclude that the most likely mechanism for oxidizing terrestrial planets is aqueous alteration of their antecedent planetesimals, both in our Solar System and beyond.

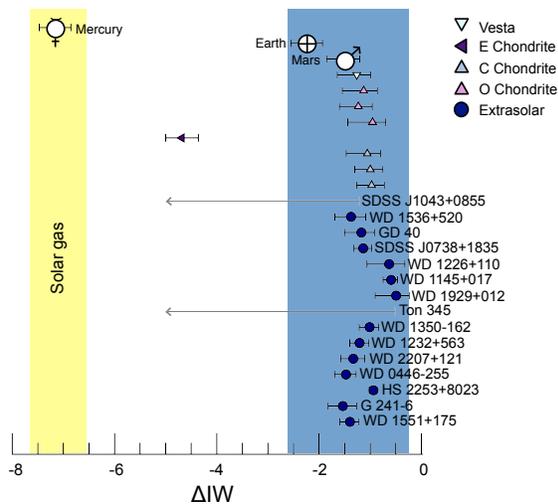


Fig. 1 ΔIW values of rocks polluting WD stars compared with Solar System rocks representing planets and asteroids (Doyle et al., in prep.).

ΔIW values of extrasolar rocks: We use the mole fractions of FeO (x_{FeO}) for rocks accreted to polluted white dwarf stars to calculate the fugacity of oxygen of these rocks relative to the IW reference (from $\Delta IW = \log f_{O_2} - \log f_{O_2}(IW) = 2\log(x_{FeO}/0.85)$ where 0.85 is $\sim x_{Fe}$

in the metal). Our most recent results (Fig. 1) reinforce the conclusion that the majority of accreted extrasolar rocks are similar to carbonaceous chondrites with ΔIW values of about -1 .

Sources of oxidation: Increasing the fugacity of oxygen from that of a solar-like gas to values typical of rocks requires an efficient means of eliminating H relative to O. Candidate mechanisms are described briefly below.

Oxidation in the protoplanetary disk: In our solar system there is evidence for oxidation of rocky material during the earliest stages. This evidence includes oxidation from solar-like f_{O_2} in CAI interiors to more typical chondrite-like values in Wark-Lovering rims [2] as well as significant concentrations of FeO in typical chondrite matrix silicate grains. While oxidation in the disk evidently occurred at least locally, widespread oxidation requires enhancement in H_2O/H_2 by a factor of about 400 at temperatures sufficient for reaction with silicate dust [3]. A mechanism accomplishing both has yet to be proposed in detail.

Oxidation associated with core formation. It has been proposed that FeO of Earth's mantle, and by inference those of other terrestrial planets, could increase as Si enters the metallic core. There are two basic mechanisms for reducing silicate Si: 1) $2Fe^0 + Si^{4+} \rightarrow Si^0 + 2Fe^{2+}$; and 2) $2O^{2-} + Si^{4+} \rightarrow Si^0 + 2O^0$. The former results in addition of FeO to the mantle and no O to the core, raising the apparent intrinsic f_{O_2} of the mantle. The latter adds Si and O to the core with no change in mantle FeO. We introduce a 2D cartesian reaction space representing the different paths for adding Si to the core (Fig. 2). Fig. 2 shows that the concentrations of O and Si in the core of a planet (e.g., Earth) could be used to assess the amount of FeO introduced to the mantle by core formation. However, studies differ on these values, making the efficacy of this process unclear. Disproportionation of Fe^{2+} to Fe^{3+} and Fe^0 in planet mantles would increase calculated f_{O_2} but requires high pressures and cannot explain asteroid oxygen fugacities. The additional reaction $Fe + H_2O \rightarrow 2H^0 + FeO$ could also add FeO to an initially wet mantle, but the H solubility in metallic cores remains poorly constrained at relevant conditions.

Regardless, increasing mantle FeO solely by core formation does not explain the oxidation of protoplanetary chondritic material. Nor does it offer a comprehensive explanation for the relatively oxidized

compositions of extrasolar rocks polluting WDs; rocky bodies accreted to WD stars are estimated to have had masses corresponding to large asteroids rather than planets, although precise mass estimates are model dependent [4].

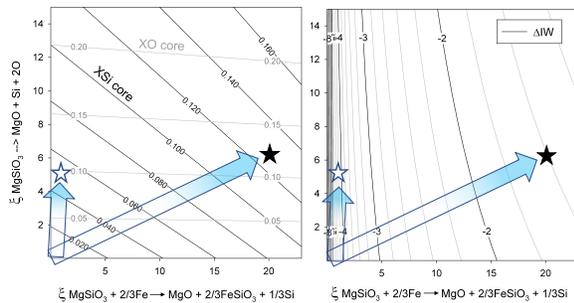


Fig 2. 2D reaction space depicting mechanisms for introducing O and/or Si to the metallic core of a body during core formation. Contours for mole fractions of Si and O in the core (left) and calculated f_{O_2} from FeO in the mantle (right). ξ represents molar progress of the two basis vector reactions shown. The open and closed stars correspond to projections of the estimated core compositions from [5] and [6], respectively.

Oxidation by aqueous alteration. The evidence for aqueous alteration of rocks representing the building blocks of the terrestrial planets in the Solar System is plentiful in meteorites and in extant bodies, including Ceres and Enceladus. The principal water-rock reaction is similar to $Mg_{1.8}Fe_{0.2}SiO_4 + 1.37H_2O \rightarrow 0.5Mg_3Si_2O_5(OH)_4 + 0.3Mg(OH)_2 + 0.067Fe_3O_4 + 0.067H_2$ and is an efficient means of separating H from O upon outgassing of the evolved H_2 gas. Based on the ubiquity of ^{26}Al as a heat source in star-forming regions [7], this reaction is expected to be inevitable for water-bearing planetesimals of all sizes accreted $> \sim 2$ Myrs after disk formation as well as for bodies accreted earlier but no larger than about ~ 5 km in radius (Fig. 3). Therefore, aqueously altered planetesimals are expected to be an important source of oxidized iron for rocky bodies of all scales, from asteroids to large rocky planets.

Internal heating ensures that the water-rock reactions liberating H_2 occur in bodies accreted over a wide range of radial distances from their star. Evidence is mounting that primitive rocks comprising the innermost Solar System resembled the relatively dry enstatite chondrites (e.g., Mercury) and that bodies in the outer Solar System harbored the water ice that resulted in aqueous alteration. However, elemental abundances in the mantles of Earth and Mars require that their mantles evolved chemically in response to accretion of

progressively more oxidized material simultaneous with core formation. The late accreted materials apparently delivered FeO like that found in most chondrite groups [6]. Late accretion of oxidized planetesimals is consistent with their relatively large radial distances from their host star.

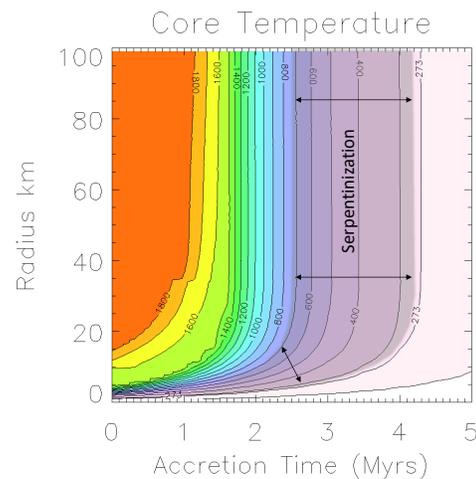


Fig 3. Compilation of updated planetesimal thermal models showing contours of peak temperatures vs. radius of the body and accretion time relative to an initial $^{26}Al/^{27}Al$ of 5×10^{-5} (McCain and Young, unpub.). Temperature isotherms are in degrees Kelvin.

Conclusions: We find that of the possible mechanisms for oxidizing rocky materials in general, aqueous alteration of planetesimals is the most likely. Aqueously altered planetesimals were important sources of FeO in our Solar System and the same is evidently true in other planetary systems.

In effect, the polluted WDs are evidence for the importance of water in the evolution of terrestrial planet precursors throughout the Galaxy.

References: [1] Doyle A.E. et al. (2019) *Science* 366, 356-359. [2] Dyl K.A. et al. (2011) *GCA* 75, 937-949. [3] Monteux J. et al. (2018) *Space Science Reviews* 214. [4] Jura M. and Young E.D. (2014) *Annual Review of Earth and Planetary Sciences* 42, 45-67. [5] Badro J. et al. (2015) *PNAS* 112, 12310-12314. [6] Rubie D.C. et al. (2015) *Icarus* 248, 89-108. [7] Jura M. et al. (2013) *ApJL* 775, L41.