



# Evidence of magmatic degassing in Archean komatiites: Insights from the Wannaway nickel-sulfide deposit, Western Australia



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## ABSTRACT

Magmatic degassing from komatiite lava flows potentially influenced the geochemical evolution of the Archean atmosphere and hydrosphere. We argue that the escape of SO<sub>2</sub>-rich volatiles from komatiites impacted on the mineralogical, geochemical and isotopic composition of associated nickel-sulfide mineralization leaving behind detectable and measurable footprints that can be best observed where the polarity of the magmatic sequence is clearly recognizable. Here we focus on the ore-bearing sequence of the Archean komatiite-hosted N01 nickel-sulfide orebody at Wannaway, Yilgarn Craton, Western Australia. This deposit displays a volcanic sequence with a well-defined succession of stratigraphically-correlated facies comprising a massive sulfide horizon at the base of the channelized komatiite flow, overlain by matrix and disseminated sulfide mineralization. Pyrrhotite is the dominant sulfide phase in the lower part of the ore profile. The amount of troilite gradually increases from the base of the matrix ore over several meters up-sequence, eventually becoming dominant at the expense of pyrrhotite. In the upper portion of the mineralized sequence troilite is associated with accessory Mn sulfide alabandite (MnS), which is usually reported in reduced terrestrial and extra-terrestrial environments. Such mineralogical and volcanological features are consistent with upwards decreasing in  $f_{S_2}$  and  $f_{O_2}$  away from the basal contact of the komatiite flow. After evaluating the possible role of metamorphism, the pyrrhotite-troilite-alabandite assemblage and the progressive up-sequence decrease of the pyrrhotite/troilite ratio across the upper part of the mineralized sequence are interpreted as magmatic and indicative of progressive loss of sulfur with concomitant establishment of reducing conditions within the sulfide melt ponding at the base of the komatiite lava. In this context, the investigation of spatially constrained sulfur isotopic signatures allows to isolate the multiple sulfur fractionation processes that impacted on sulfide mineralization and ultimately permits the identification of the isotopic shift associated with magmatic degassing. Following this approach we recognize two distinct sulfur isotope exchanges processes triggered by 1) assimilation of sulfidic shales during emplacement of the komatiite flow, and 2) equilibration between the sulfide melt and the sulfur dissolved in the silicate melt. We finally correlate the remaining  $\delta^{34}S$  depletion up-stratigraphy with the loss of heavy sulfur isotopes through magmatic degassing of SO<sub>2</sub>-rich volatiles from the ultramafic flow. The emission of SO<sub>2</sub> upon emplacement and cooling of the magma flow would also explain the progressive reducing  $f_{O_2}$  and  $f_{S_2}$  conditions indicated by variations in mineral assemblages from the base of the komatiite upwards.

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## 1. Introduction

Komatiites are ultramafic rocks formed via high degrees of partial melting (up to 50%) of the mantle mostly in the Archean (Arndt et al., 2008). Consequently, komatiites provide a unique perspective on a number geological and geochemical issues including 1) the secular variation of the mantle temperature, 2) the mantle composition and 3) the transition from a hazy, greenhouse Archean Earth

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to an oxygen-rich atmosphere sustaining life (Arndt and Nisbet, 2012 and references therein). Komatiite-hosted mineralization also accounts for approximately 20% of global nickel-sulfide resources (Arndt et al., 2008). Most komatiite-hosted deposits were subjected to post-magmatic geological processes that impacted on the sulfur isotope signatures of the primary ore (Marini et al., 2011; Seal, 2006). As both magmatic and post-magmatic processes lead to mass-dependant sulfur isotope fractionation (MDF; monitored by  $\delta^{34}\text{S}$ ), the investigation of  $\delta^{34}\text{S}$  signatures alone is not sufficient for tracing the sulfur source and assessing the subsequent evolution of sulfur-bearing compounds through the complex geological history of these systems. Nevertheless, in the Archean oxygen-poor atmosphere ( $<10^{-5}$  current level) sulfur interacting with UV-rays was affected by mass-independent fractionation (MIF; here as  $\Delta^{33}\text{S}$ ), as discussed in Farquhar et al. (2000). These signatures display a chemically conservative nature as metamorphic and hydrothermal processes, or more generally equilibrium or kinetic fractionation reactions, do not alter the original  $\Delta^{33}\text{S}$  values if not through dilution (Mojzsis et al., 2003). Therefore, the combination of  $\Delta^{33}\text{S}$  and  $\delta^{34}\text{S}$  signatures in Archean environments provides a more suitable isotopic framework to disentangle the effects of subsequent fractionation processes.

MIF signatures can be related to specific Archean sulfur reservoirs: positive  $\Delta^{33}\text{S}$  values are suggestive of reduced elemental sulfur preferentially incorporated in shale-hosted disseminated sulfides, whereas negative  $\Delta^{33}\text{S}$  values mark the water-soluble oceanic sulfate reservoir likely to be involved in hydrothermal and exhalative activity (Farquhar and Wing, 2003). In this context, the application of multiple sulfur isotope systematics to komatiite-hosted sulfides has already improved the understanding of ore-forming magmatic processes. In fact, recent studies established the importance of country rock assimilation in the attainment of sulfide supersaturation (LaFlamme et al., 2016; Hiebert et al., 2016; Ripley and Li, 2013; Bekker et al., 2009) and provided a new framework for identifying the key controlling factors for the district-scale distribution of komatiite-hosted nickel sulfide deposits (Fiorentini et al., 2012).

In this manuscript, we build on this framework to document the sulfur isotope architecture of the komatiite-hosted Wannaway deposit in the Yilgarn Craton of Western Australia. New spatially referenced multiple sulfur isotope data from sulfide-bearing samples that were recently mineralogically and geochemically characterized (Moroni et al., 2017) provide compelling evidence of the interplay between multiple fractionation processes: isotope exchange reactions driven by (1) the assimilation of crustal material and (2) the equilibration between sulfide melt and sulfur dissolved in the silicate melt, (3) the degassing of sulfur dioxide ( $\text{SO}_2$ ) upon emplacement and cooling of the komatiite lava flow.

The effects of sulfur isotope exchange reactions in ultramafic mineralization were delineated by several works (e.g. Ripley and Li, 2013 and references therein), whereas the isotopic consequences of magmatic degassing of sulfur were uniquely examined in S-poor systems (e.g. Mandeville et al., 2009). In this regard, the extent and direction of the isotopic shifts accompanying the degassing of sulfur dissolved in silicate melts were modeled according to the speciation of both dissolved and degassed sulfur, temperature, pressure and amount of sulfur lost (Marini et al., 2011 for a review). These mutually dependent parameters were quantified at best through direct measures of degassing rates and volatile compositions from present-day magmatic systems (e.g. de Moor et al., 2013). In addition, Le Vaillant et al. (2017) recently revealed the significant role of sulfur degassing from the nickel-sulfide mineralization hosted in the giant Noril'sk deposits (Russia) in relation to the Permian–Triassic mass extinction event. In light of integrated mineralogical and geochemical pieces of evidence, in this paper we put forward the hypothesis that most of the multiple sulfur

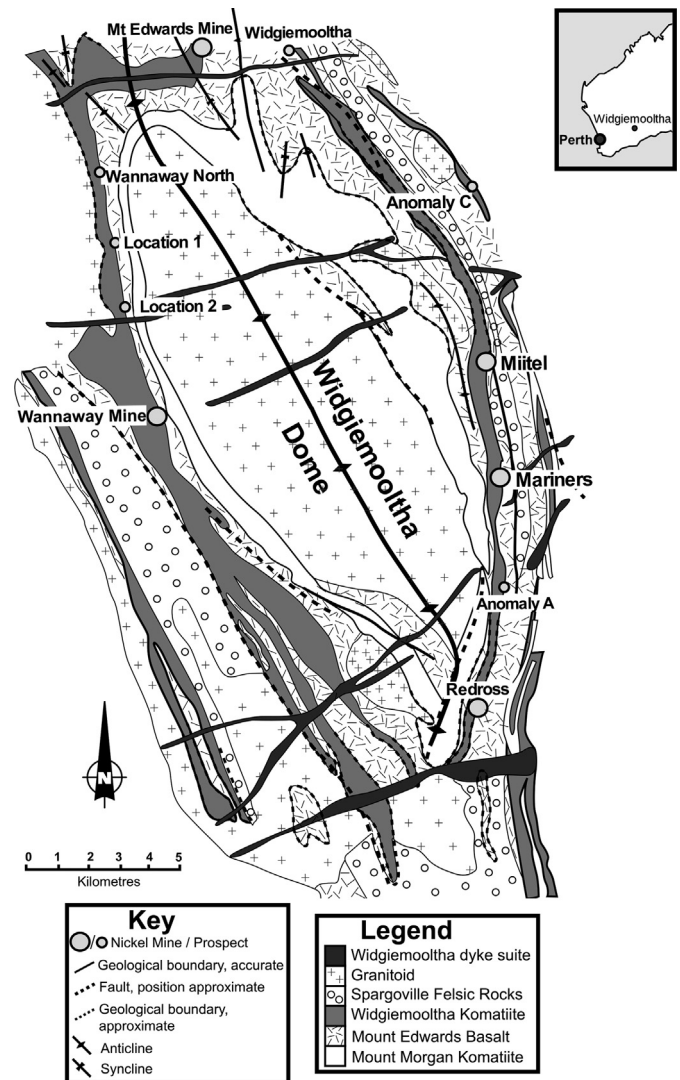


Fig. 1. Location of the Wannaway nickel-sulfide deposit and simplified geologic map of the Widgiemooltha Dome area (Seat et al., 2004; modified after McQueen, 1981b).

isotopic variations recorded at the Wannaway deposit can be best explained as a consequence of magmatic degassing of an Archean komatiite lava flow.

## 2. Geological setting

The Wannaway deposit is located on the western flank of the Widgiemooltha Dome (Fig. 1), a synkinematic granitoid diapir structure intruded into the Norseman-Kalgoorlie mafic-ultramafic succession of the Yilgarn Craton, Western Australia (McQueen, 1981a). The stratigraphy of this greenstone succession consists of a basal komatiite (Mount Morgan Komatiite) overlain by tholeiitic basalts (Mt Edwards Basalt) and then by a thick komatiite unit with intercalated sediments (Widgiemooltha Komatiite), hosting several nickel-sulfide orebodies, including Wannaway, at its basal contact (Seat et al., 2004). The entire succession underwent polyphase deformation events and metamorphism up to mid-amphibolite facies (McQueen, 1981a). Nevertheless, deformation, metamorphism, serpentinization and  $\text{CO}_2$  metasomatism developed heterogeneously throughout the dome: according to McQueen (1981b), on the west flank of the Dome, where the Wannaway deposit is situated, early serpentinization, talc-carbonate alteration and metamorphic recrystallization were patchy and localized, whereas retrogressive serpentinization was pervasive and

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