Genesis of the mafic granophyre of the Vredefort impact structure (South Africa): Implications of new geochemical and Se and Re-Os isotope data

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ABSTRACT

This contribution is concerned with the debated origin of the impact melt rock in the central uplift of the world's largest confirmed impact structure—Vredefort (South Africa). New major- and trace-element abundances, including those of selected highly siderophile elements (HSEs), Re-Os isotope data, as well as the first Se isotope and Se-Te elemental systematics are presented for the felsic and mafic varieties of Vredefort impact melt rock known as "Vredefort Granophyre." In addition to the long-recognized "normal" (i.e., felsic, >66 wt% SiO_2) granophyre variety, a more mafic

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(<66 wt% SiO$_2$) impact melt variety from Vredefort has been discussed for several years. The hypothesis that the mafic granophyre was formed from felsic granophyre through admixture (assimilation) of a mafic country rock component that then was melted and assimilated into the superheated impact melt has been pursued here by analysis of the two granophyre varieties, of the Dominion Group lava (actually meta-lava), and of epidiorite mafic country rock types. Chemical compositions, including high-precision isotope dilution–derived concentrations of selected highly siderophile elements (Re, Os, Ir, Pt, Se, Te), and Re-Os and Se isotope data support this hypothesis. A first-order estimate, based on these data, suggests that some mafic granophyre may have resulted from a significant admixture (assimilation) of epidiorite to felsic granophyre. This is in accordance with the findings of an earlier investigation using conventional isotope (Sr-Nd-Pb) data. Moreover, these outcomes are in contrast to a two-stage emplacement model for Vredefort Granophyre, whereby a mafic phase of impact melt, derived by differentiation of a crater-filling impact melt sheet, would have been emplaced into earlier-deposited felsic granophyre. Instead, all chemical and isotopic evidence so far favors formation of mafic granophyre by local assimilation of mafic country rock—most likely epidiorite—by a single intrusive impact melt phase, which is represented by the regionally homogeneous felsic granophyre.

INTRODUCTION

The Vredefort impact structure in north-central South Africa has been known for decades as the largest confirmed impact structure in the world (e.g., Gibson and Reimold, 2008; Reimold and Koeberl, 2014; Gottwald et al., 2020). At 250–300 km original diameter, this structure encompasses the entire erosional remnant of the economically important Witwatersrand Basin. The currently exposed surface of the Vredefort Dome (Fig. 1), in the geographical center of the basin, represents a deep cross section through the central uplift of this huge, complex impact structure. The Witwatersrand Basin itself forms the remnant of the ring basin around the central uplift structure (for a review of the macroscopic features of the Vredefort impact structure, see, e.g., Gibson and Reimold, 2008; Grieve et al., 2008). The latter work places the Vredefort impact structure into context as a likely multiring impact structure, together with Sudbury (Canada), which has an estimated original diameter of 250 km (e.g., Lightfoot, 2016), and Chicxulub (México), which has an estimated original diameter of 180–200 km (e.g., Gulick et al., 2019).

The Vredefort impact structure is also one of the oldest confirmed impact structures on Earth, with an age of 2.023 ± 0.004 Ga determined by the U-Pb method on zircon (Kamo et al., 1996; for a review of other age dating, see Gibson and Reimold, 2008; Erickson et al., 2011, 2013; Gottwald et al., 2020). The Vredefort and Sudbury impact structures represent the oldest recognized, demonstrably large impact events on our planet.

The Vredefort Dome is host to two types of impact-generated melt rock. The first is so-called pseudotachylitic breccia, which occurs on the dome in numerous centimeter- to decimeter-scale veins and pods, besides much larger, 100-m-scale to kilometer-scale occurrences (e.g., on the Otavi and Abel farms in the northeastern sector of the dome) that have been well documented by,

e.g., Dressler and Reimold (2001), Reimold and Gibson (2006), and Gibson and Reimold (2008). Some of the very large exposures of pseudotachylytic breccia represent dikes. Other large exposures can be studied, in part in three dimensions, in a number of quarries. Originally, these rocks were termed pseudotachylyte (Shand, 1916). The modern spelling pseudotachylite has since been applied in a large number of investigations of this enigmatic rock type from Vredefort and Sudbury (there represented by the so-called Sudbury Breccia), and other impact structures where only comparatively small occurrences of such material have been recognized. However, the term "pseudotachylite" is reserved in the field of structural geology for friction melt rock. Friction melting can certainly take place during the ultradynamic impact cratering process, but a range of other processes has been invoked in the discussion about the formation and emplacement of this melt rock at Vredefort—and the even more voluminous occurrences of Sudbury Breccia in the less eroded Sudbury structure. For this reason, Reimold (1998) coined the term "pseudotachylitic breccia" as a nongenetic option to be used as long as the true mode of origin of such an occurrence is not constrained fully. Recently, the origin of these melt breccias was the subject of a first Sr-Nd-Pb isotopic investigation, which strongly supported local derivation from melting of country rock at a given site (Reimold et al., 2017). This is in agreement with much petrographic and especially all chemical findings accumulated over the past decades (e.g., Reimold et al., 2006; for a review, see Reimold et al., 2017) and does not support a previous idea by Lieger et al. (2011) that large pseudotachylitic breccia occurrences represent impact melt injections.

The second impact-generated melt rock type of the Vredefort Dome, the main topic of this study, occurs in the form of nine several-kilometer-long and up to 50-m-wide dikes of so-called Vredefort Granophyre (e.g., Therriault et al., 1996, 1997;

Reimold and Gibson, 2006). These dikes are generally accepted as representing impact melt rock that intruded downward along deep fractures in the central uplift, from an original reservoir within the crater cavity. To date, these dikes are exposed in a deep profile through the remnant of the central uplift, exhumed after prolonged erosion to an estimated depth of 7–10 km (McCarthy et al., 1990; Gibson et al., 1998). Here, we refer to Vredefort Granophyre, or just granophyre, as the general term for the Vredefort impact melt rock, without distinction of whether the mafic or the felsic variety is meant.

In recent years, a controversy has centered on the style of emplacement of the Vredefort Granophyre, with two groups favoring contrasting models. Lieger (2011), Lieger et al. (2011), and Lieger and Riller (2012) suggested that two consecutive intrusive events, consisting of, first, a felsic granophyre phase,

and then a second, more mafic phase, could be found at Vredefort, in analogy to the composite Offset Dikes of the Sudbury structure (see also Kovaleva et al., 2019). The only direct evidence for these two phases is known from the Kopjeskraal farm in the outer northwest sector of the core of the Vredefort Dome (Fig. 2), where indeed the felsic granophyre carries a second, more mafic phase. It was also suggested that similar mafic granophyre could occur on Rensburgsdrif farm to the southwest of Kopjeskraal but on the opposite (southern) bank of the Vaal River. However, to date, this has not been well documented and, thus, is still subject to further investigation. In previous research on the regional granophyre occurrences, several chemical analyses for samples with <66 wt% SiO_2 were obtained, although comparatively rarely (e.g., Willemse, 1937). Wannek (2015) and Reimold et al. (2017) presented chemical and isotopic evidence that countered this
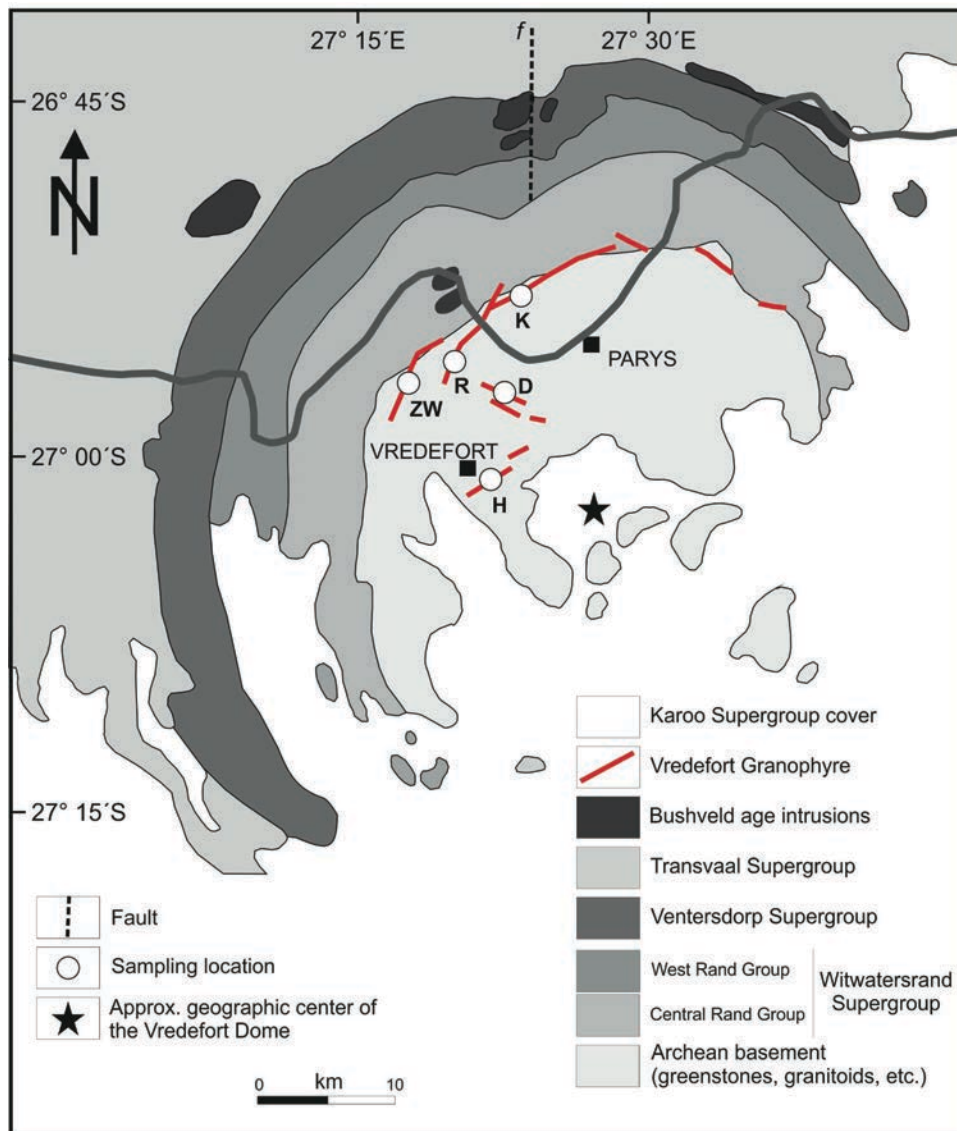

Figure 1. Schematic geology of the Vredefort Dome and approximate locations of granophyre dikes (based on Therriault et al., 1997) and locations of samples utilized in this study: K—Kopjeskraal, D—Daskop, H—Holfontein, R—Rensburgsdrif, ZW—Zuid Witbank (more detail on sampling locations is given in the text).
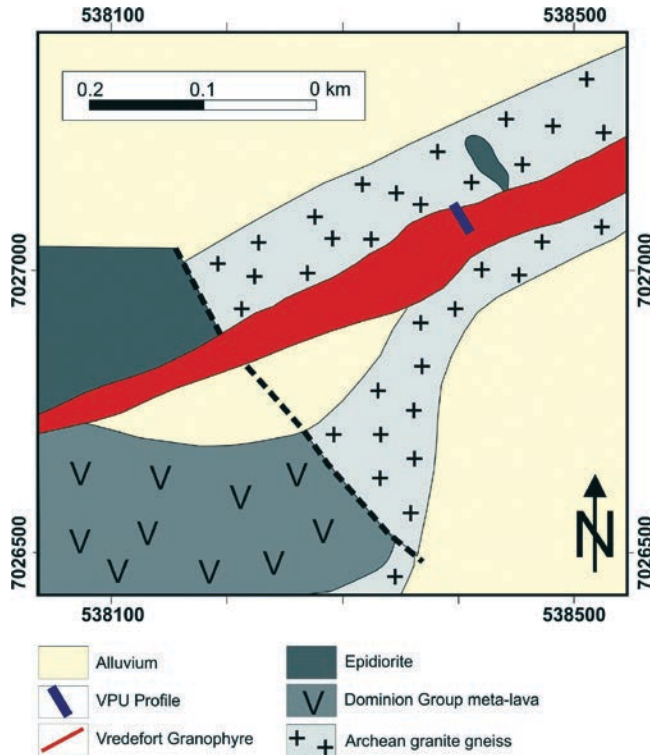
Figure 2. Schematic geological map of the area around the section of the granophyre dike sampled for this study on Kopjeskraal farm (after Wannek, 2015). See text for further detail. Sampling profile refers to the suite of VPU samples (see also Table 1B). Coordinate system: UTM Hartebeesthoek 94.

twofold injection hypothesis. Instead, their work supported the idea that mafic granophyre only occurs where the felsic dikes cut across or occurred adjacent to mafic country rock (principally the so-called epidiorite; see below). At such locations, a granophyre dike could locally assimilate such a mafic component during its emplacement. This idea was already advanced by Therriault et al. (1997) and subsequent workers (see review by Reimold and Gibson, 2006).

This ongoing controversy about the origin and emplacement of felsic and mafic granophyre is at the center of the present investigation. We analyzed several samples of mafic and felsic granophyre for their chemical compositions. In particular, samples from a traverse across a major portion of the granophyre dike on Kopjeskraal were analyzed. The objective for this work was to further investigate the spatial and chemical relationships between felsic and mafic granophyre, on the one hand, and among felsic granophyre, mafic granophyre, and epidiorite country rock, on the other hand. Abundances of highly siderophile elements and Re-Os and Se isotopic compositions were determined for a range of felsic and mafic granophyre samples, as well as for epidiorite and a second mafic

intrusive rock from Kopjeskraal—a meta-lava of the Dominion Group (e.g., Jackson, 1994).

The Re-Os isotope and first Se isotope and Se-Te elemental systematics were used to trace a possible mafic component that might have been assimilated by felsic granophyre. These new results do not support the two-stage infiltration model for the generation of Vredefort impact melt rock. They are, however, consistent with the hypothesis that favors the local admixture of epidiorite to felsic granophyre to generate the mafic granophyre.

GEOLOGICAL BACKGROUND

The Vredefort impact structure is centered ~120 km to the southwest of Johannesburg, South Africa. It extends over the entire region known as the Witwatersrand Basin in the central part of the Kaapvaal craton. The Vredefort impact structure consists of the Vredefort Dome, a structural uplift feature of, at the current exposure level, ~90 km width, and the surrounding basin, which to the north of the dome attains a maximum depth of some 13 km (Henkel and Reimold, 1998; Gibson and Reimold, 2008). The geophysical modeling by Henkel and Reimold (1998) also established the current size estimate for the original impact structure of some 250 km or perhaps even more. The Vredefort Dome is well exposed in its northern and northwestern parts but largely obscured by strata (shale and dolerite sills) of the Phanerozoic Karoo Supergroup in the southern sectors (Fig. 1). The core of the Vredefort Dome is ~40–45 km wide and composed of Archean gneisses and migmatites that range in age from ca. 3.15 to 3.07 Ga (Gibson and Reimold, 2008; Gibson, 2019; and references therein). These basement rocks were generated during a high-grade (upper amphibolite to granulite facies) dynamothermal metamorphic event (Lana et al., 2003, 2004; Armstrong et al., 2006; Gibson and Reimold, 2008; Gibson, 2019). The main rock types identified are trondhjemitic and granodioritic gneisses and granites, with subsidiary mafic, ultramafic, meta-pelitic, and meta-ironstone xenoliths (Gibson and Reimold, 2008). The innermost part of the core exhibits rocks of granulite metamorphic grade, whereas the outer part comprises amphibolite facies granitoids.

This basement core is surrounded by a 20–25-km-wide collar of subvertical to overturned, late Archean to early Paleoproterozoic supracrustal strata of the Dominion Group (which, in the region of the Vredefort Dome, is represented by a fine-grained, mafic metavolcanic unit, which we refer to here as Dominion Group meta-lava), Witwatersrand Supergroup (clastic metasedimentary rocks), Ventersdorp Supergroup (meta-dolerite, in the Vredefort literature referred as "epidiorite," the term used here as well; cf. Gibson and Reimold, 2008), and Transvaal Supergroup (carbonates and subsidiary argillites and arenites). This stratigraphic succession was deposited between ca. 3.07 and ca. 2.1 Ga (Armstrong et al., 1991; Gibson, 2019). From the core-collar contact outward, the supracrustal rocks exhibit lower amphibolite and then greenschist metamorphic grade.

The many sills of so-called epidiorite occurring in the collar of the Vredefort Dome have been considered as possible feeder dikes for the craton-wide deposition of the (now metamorphosed) lavas of the 2.7 Ga Ventersdorp Supergroup (Pybus, 1995; Reimold et al., 2000). Besides these Ventersdorp Supergroup–related sills, the basement rocks and supracrustal strata also contain intrusive occurrences of tholeiitic rock linked to the 2.06 Ga Bushveld magmatism, and several alkaline or mafic intrusive bodies that occur within or at the circumference of the collar and have ages that also link them with the Bushveld magmatism. In the north-central part of the core of the Vredefort Dome occurs a ca. 1.05 Ga monzodiorite sheet (Reimold et al., 2000).

The deep erosion of the Vredefort impact structure has led to the removal of the entire impact breccia fill of the large crater structure and exposed the current deep profile through the central uplift. As, for example, demonstrated by the geophysical modeling of Henkel and Reimold (1998) and consistent with the metamorphic grades of the basement rocks exposed in the core (e.g., Gibson and Reimold, 2005) and the numerical modeling of Ivanov (2005), the granitoids and the xenoliths within them represent original midcrustal levels that were exhumed from their original settings at ~−15 to −25 km depth, from the core-collar contact to the center of the dome (R.L. Gibson, University of Witwatersrand, 2020, personal commun.).

Several U-Pb dating studies on zircon and monazite, also from the two types of impact-generated melt rock (pseudotachylitic breccia and granophyre), have been carried out (Kamo et al., 1996; Moser, 1997; Gibson et al., 1997; cf. also Erickson et al., 2011). The age obtained by Kamo et al. (1996) of 2.023 ± 0.004 Ga has been widely accepted and quoted ever since as the age of the Vredefort impact event (e.g., Earth Impact Database, accessed July 2020; Gottwald et al., 2020).

BACKGROUND ON
THE VREDEFORT GRANOPHYRE

The Vredefort impact melt rock (Reimold and Gibson, 2006; Gibson and Reimold, 2008) occurs in the Vredefort Dome in the form of nine dikes of a fine-grained melt rock with a micropegmatitic groundmass that lent the lithology the name granophyre (e.g., Therriault et al., 1996, 1997; Reimold and Gibson, 2006). Four of these dikes are emplaced in the Archean gneiss basement, the core of the Vredefort Dome, whereas the others straddle the core-collar boundary in a semi-arc from the west to the northeast (as schematically indicated on Fig. 1). The four dikes in the core extend in NE-SW and NW-SE directions (roughly radially with respect to the center of the dome), which are also the principal directions of the regional fabric (gneissosity) of the core of the dome. The core-collar boundary dikes have straight to more sigmoidal geometries. They do not extend strictly tangential to the core but locally transgress from the core into innermost supracrustal strata of the collar. The dikes are, along their extension, variably several meters (toward their terminations on surface) to several decameters wide, and they are up to several kilometers

long. Since the earlier work of the 1990s, it has been discussed that the tapering endings of the dikes, as well as narrow apophyses off the dikes, suggest that these dikes have limited continuation into the basement. This was recently supported by the work of Fourie et al. (2019) through geophysical measurements at one of the core dikes.

The granophyre dikes consistently display clast populations predominantly composed of material from the Archean granite-gneiss basement, with significant contributions from Witwatersrand Supergroup quartzite and, comparatively much rarer, shale (Reimold et al., 1990; and later workers). Clasts derived from other lithologies are exotic; in particular, mafic clasts have only ever been described from locations where such rare clasts could be linked to mafic lithologies occurring within less than 50 m distance from the inclusion observation (e.g., Therriault et al., 1996; Reimold and Gibson, 2006, and references therein). This particularly pertains to sites along the core-collar boundary, where both the Ventersdorp Supergroup–related epidiorite and the Dominion Group meta-lava occur in outcrop and form possible sources for these rare mafic clasts (cf. the following section).

The mineralogical composition of the granophyre is dominated by orthopyroxene (hypersthene), plagioclase and K-feldspar, and quartz; biotite and amphibole, as well as iron-titanium oxides, are important minor phases. Quartz and feldspars ubiquitously form micrographic intergrowths, occurring both within the matrix and within clasts of granitoid precursors that were partially melted after entrainment into superheated impact melt. Two types of textures are typical for the Vredefort Granophyre: a spherulitic variety and a granular variety, whereby in the former case, orthopyroxene laths frequently form rosettes/spherulites, in contrast to the second variety, in which orthopyroxene forms more short-prismatic, stubby crystals of random orientation. There is abundant petrographic evidence showing that the microgranophyric intergrowths of the groundmass were formed at the expense of granitic precursor material. Mineral clasts are quite rare. Occasionally, relics of feldspar crystals can be observed as part of the matrix. Most lithic clasts are generally, but not always, entirely annealed (recrystallized) to mosaic-textured quartz, or transformed to checkerboard feldspar and vermicular quartz (Buchanan and Reimold, 2003). It took a long time and the study of many thin sections of granophyre samples to discover shock evidence in quartz. Shocked quartz was discovered in granophyre samples by Buchanan and Reimold (2003), and shocked zircon was identified in granophyre samples by Leroux et al. (1999) and Kamo et al. (1996). Since then, shocked monazite from Vredefort-derived sediment deposits has been added to the impact evidence for this structure (Erickson et al., 2013). A very small meteoritic component in granophyre samples was found by Koeberl et al. (1996) through application of the Re-Os isotope method.

Most recently, electron backscatter diffraction (EBSD) evidence for the former presence of reidite—the high-pressure phase of $ZrSiO_4$ formed under shock conditions in the pressure range from 20 to 40 GPa (Leroux et al., 1999)—was reported

in the form of FRIGN ("former reidite in granular neoblastic") zircon from Vredefort Granophyre by Kovaleva et al. (2018). It is now safe to say from the collective evidence that the clast content of the Vredefort Granophyre involves material from various parts of the evolving transient cavity, with the clast populations studied containing particles of a range of shock stages, from unshocked to 20–40 GPa (formation of multiple sets of planar deformation features in quartz and of reidite) to >40 GPa, when target rock clasts were partially or completely melted (for further information on progressive shock metamorphism, see, e.g., Stöffler et al., 2018).

Vredefort Granophyre at Kopjeskraal and Rensburgsdrif Farms, NW Vredefort Dome

Mafic clasts have only been reported very rarely from the four dikes within the Archean gneiss complex, which are located far from any mafic intrusive bodies. Also, the dikes along the core-collar boundary have not shown many mafic clasts (e.g., Therriault, 1992; Therriault et al., 1996).

In the northwestern sector of the Vredefort Dome, along the core-collar boundary, a rather wide granophyre dike (locally, its width exceeds 50 m) extends over 850 m on the Kopjeskraal Lodge property (on the Iniekom farm; see Gibson and Reimold, 2008), cutting locally along its strike through Archean granitoid (Fig. 2). This figure illustrates that a significant fault displaces the local stratigraphy to the southwest of the dike, according to Wannek (2015) by 300–400 m. Epidiorite is prominent to the northwest of the sampled section of the dike, where this mafic lithology actually occurs in contact with the dike (Fig. 2). In addition, a small inlier of epidiorite was identified by Wannek ~50 m to the northeast of the sampling area, also in contact with the granophyre dike.

The Dominion Group meta-lava is also exposed at a number of places on this property, notably with excellent exposures in the vicinity of the Kopjeskraal homestead, some 650 m from our granophyre sampling area (C. Meyer, Kopjeskraal Lodge, 2020, personal commun.). Some 300 m to the southwest of the sample traverse Dominion Group meta-lava occurs. Further southwest, it is actually in direct contact with the dike. Thus, it could not be excluded, a priori, that this second mafic lithology could also have been incorporated into the impact melt, which is the reason why the meta-lava was also part of the present work. It is also worth noting that the granophyre dikes intruded into the country rocks from above, and, obviously, there is no information available as to the lithologies the impact melt may have encountered and sampled during its descent.

Note that the granophyre dikes and epidiorite intrusions have different structural forms. Epidiorite has intruded between and into the, at pre-impact time, more-or-less subhorizontal Witwatersrand strata. Thus, they initially formed sheet-like sills. However, as a consequence of the formation of the central uplift of the impact structure, these strata, including the epidiorite sills, were upturned or even overturned. The granophyre only intruded

vertically downward after this upturning event had been achieved, and, consequently, it is correct to talk about granophyre dikes. Wannek (2015) carried out fieldwork in this northwestern area of the outer core of the Vredefort Dome, which included comprehensive sampling of the dike at Kopjeskraal for petrographic and geochemical studies.

An indication was published by Lieger (2011) that a granophyre phase that was more mafic than the typically felsic granophyre (quasi-granodioritic in terms of silica content) occurred also on Rensburgsdrif farm. The northeastern section of this granophyre dike also extends into epidiorite, in the vicinity of the Vaal River bed. Along the further dike extension to the southwest of the Rensburgsdrif farmhouse, a several-decameter-wide epidiorite occurrence runs parallel to, and at a distance of <70 m from, the impact melt rock. Wannek (2015), as well as Reimold et al. (2017) in their initial isotope study of Vredefort Granophyre, which included analyses of both granophyre phases, referred to felsic granophyre and a "hybrid." The latter term denoted the mafic variety; as stated above, in the present work, we refer to felsic granophyre and mafic granophyre, respectively.

Epidiorite, as well as felsic and mafic granophyre samples from Kopjeskraal, can have a similar textural appearance. This also pertains to the respective clast populations (Wannek, 2015); however, clast abundance is very different and comparatively much enhanced in the granophyre. Epidiorite carries a clast content that is dominated by annealed quartzite clasts, besides rare shale. It can, thus, be assumed that these materials were derived from the Witwatersrand Supergroup. A relatively fine-grained epidiorite variety essentially displays the same microtexture as the granophyre, although the mineral compositions are very different (with epidiorite, for example, being dominated by amphibole instead of orthopyroxene). A clear distinction between these two lithologies in the field is in some cases difficult to impossible; however, it is our interpretation that the comparatively more mafic epidiorite occurs in the form of centimeter- to decimeter-sized dark clasts in the felsic granophyre (Fig. 3). It is obviously desirable to confirm this observation in the future by chemical analyses of such clasts. The mafic inclusions in the dike typically appear to be somewhat coarser grained than the fine-grained, rather homogeneous granophyre groundmass. These inclusions are angular to subrounded and sometimes show elongated "tails." Schlieren of apparently plasticized mafic clast material have been observed at Kopjeskraal (Wannek, 2015) and Rensburgsdrif (unpublished observations, 2019, by our team).

The origin of the Vredefort Granophyre was initially discussed in terms of endogenic processes (magmatism) (because the term granophyre was all inclusive in the past, not differentiating various felsic or mafic phases; for reviews, see Reimold and Gibson, 2006; Gibson and Reimold, 2008). For example, Bisschoff (1972) considered this lithology as a lamprophyric intrusive phase. In the 1990s, the chemical composition of the granophyre (at that time, only the felsic chemical variety was recognized) was modeled as mixtures of possible target rock combinations. French et al. (1989) and French and Nielsen (1990)

obtained a sizable (up to 80%) basaltic component in their melt mixture calculations, which they took as equivalent to the regionally important Ventersdorp Supergroup meta-lavas. An 80% component of such material was, however, deemed questionable on kinetic grounds (Reimold et al., 1990), and the paucity of clasts from mafic precursor in the granophyre clast population reported by them posed a problem as well. These authors also discussed whether the unquestionably prevalent Transvaal Supergroup dolomites and arenitic rocks of the target sequence could have been implicated in the formation of the granophyre, for which there is no indication in the clast population either. The carbonate target rock would in all likelihood have been dissociated upon impact. Therriault et al. (1997) discussed whether or not it was inevitable that a clast population of an impact melt rock had to mirror the pre-impact target composition. Reimold et al. (1990) obtained a good fit for a mixture of granitoid akin to the Archean basement in the dome with quartzite and shale from the Witwatersrand Supergroup with the chemical composition of felsic granophyre, in analogy to the principal clast population observed regionally in granophyre samples.

SAMPLING

The granophyre samples previously used for the Re-Os isotope study by Koeberl et al. (1996) and for the present study were derived mainly from the northwestern dike where it cuts across the Kopjeskraal property (K in Fig. 1). Samples BG-168 and BG-10 originated from the granophyre dike cutting across the

Figure 3. Field impressions of Vredefort Granophyre dikes with mafic inclusions. (A) Exposure of the dike on Kopjeskraal, with several up to decimeter size clasts in felsic granophyre. This includes several granite clasts (lighter colored) in the bottom part of the image, as well as several (sub)angular mafic clasts in the upper and middle parts. In the field, these mafic clasts showed variable grain sizes, though always slightly enhanced compared to surrounding groundmass. Image is courtesy of Ana Rita Maciel. Pen for scale ca. 13 cm long. (B) An ~70-cm-wide exposure of granophyre on the Kopjeskraal property, with a host of subrounded to angular clasts of several centimeters to decimeters in size. The clasts are clearly distinguished from the slightly darker groundmass of the dike by their slightly elevated relief and subtle color difference. The clasts have a slightly larger grain size than the granophyric groundmass. We interpret these inclusions as relics of epidiorite that were not assimilated by felsic granophyre. The exposure is about 1 m wide. (C) Block of felsic granophyre on Rensburgsdrif farm, with a decimeter-sized clast of epidiorite. Hammer, for scale, is ~35 cm long.

Rensburgsdrif and Zuid Witbank farms (ZW in Fig. 1; 26°54′S, 27°21′E), sample BG-4 is from the Daskop locality (D in Fig. 1; 26°57′S, 27°24′E) within the Archean core, and samples BG-7 and BG-9 are from Holfontein (H in Fig. 1; 27°01′S, 27°23′E) (also in the core).

All samples denoted "DW" or "VPU" are from the Kopjeskraal property. The DW samples are from Wannek (2015). The VPU profile was sampled ~30 m south of the site with large epidiorite inclusions between longitudes 27°23′10.487″E and 27°23′12.191″E and latitudes 26°52′39.588″S and 26°52′40.269″S, starting with the granite sample just outside of the northwestern edge of the dike. This traverse covered a little more than half the width of the dike, which at this location is ~45 m wide. Sample spacings were on the order of 1.6–2 m. The profile, thus, extended to a little further than the middle of the dike. From then on, the dike is thickly covered with dense vegetation that prohibited further extension of the traverse. The epidiorite sample was obtained at location 27°23.2′S, 26°52.6′E, and the Dominion Group meta-lava sample came from the prominent outcrop a few tens of meters just east of the Kopjeskraal homestead.

The granophyre sample collected near the dike contact with host granite gneiss on Kopjeskraal (VPU-5) exhibits a quench texture in thin section, with microcrystals forming garben and sheaths of needle- and lath-shaped orthopyroxene and feldspars occurring in a flow-structured aphanitic mesostasis. Here, too, clasts are essentially felsic, but some clasts are filled with light brownish phyllosilicate, which could be an alteration product after a mafic lithology. A main site of the mafic granophyre on Kopjeskraal with mafic clasts is located at 26°52′50.534″S, 27°23′10.452″E. In thin section, it was not possible to distinguish between mafic inclusions and granophyric groundmass, as the epidiorite had a very similar texture with micropockets of micropegmatitic intergrowths as well. Two samples from the Rensburgsdrif/Zuid Witbank granophyre dike were analyzed in this study as well to test the possibility that a mafic granophyre phase may occur there as well (as suggested by Lieger, 2011; Lieger and Riller, 2012).

Samples for the present isotope study included three samples of the mafic granophyre, two of the felsic granophyre, and two mafic country rocks (one epidiorite sample and one Dominion Group meta-lava sample). We included sample BG-168 from Koeberl et al. (1996) in the present study to compare their result from 1996 with our new value; this sample had been interpreted by these authors to be devoid of an extraterrestrial admixture (based on an only slightly suprachondritic initial $^{187}Os/^{188}Os$ isotope composition).

METHODOLOGY

X-Ray Fluorescence Spectrometry

Samples were powdered using an agate mill. X-ray fluorescence spectrometry (XRF) was carried out with a Bruker AXS S8 TIGER instrument at the Museum für Naturkunde, Berlin. Typically, some 7–10 g of powder were analyzed per sample. Concentrations of major elements were determined on glass tablets prepared from 0.6 g of dried (4 h at 105 °C) sample powder and 3.6 g of dilithium tetraborate ($Li_2B_4O_7$) (BRA A10 Specflux) flux material. Accuracy and precision values were ~0.5 wt% for SiO_2; 0.1 wt% for Al_2O_3; 0.05 wt% for Fe_2O_3, MgO, CaO, Na_2O, and K_2O; and 0.01 wt% for TiO_2, MnO, and P_2O_5. Detection limits were 1.0 wt% for SiO_2; 0.5 wt% for Al_2O_3; 0.05 wt% for Fe_2O_3; and 0.01wt% for TiO_2, MnO, MgO, CaO, Na_2O, K_2O, and P_2O_5. About 1 g of dried sample powder was used to determine loss on ignition (LOI). For this purpose, the samples were heated in a porcelain crucible for 4 h at 1000 °C. LOI was calculated using the weight difference before and after heating. Trace-element abundances were determined on pressed powder tablets. Details on reference materials for routine XRF analysis at the Museum für Naturkunde, Berlin, were given by Raschke et al. (2013).

Platinum Group Element (PGE) Concentrations and Re-Os Systematics

An 0.4 g aliquot of bulk powder was spiked with a mixed tracer composed of ^{185}Re, ^{190}Os, ^{191}Ir, and ^{194}Pt isotopes and digested in 7 mL of inverse aqua regia (HNO_3-HCl: 5 + 2.5 mL) at 250 °C and 100–130 bar in an Anton-Paar high-pressure asher for 12 h. After digestion, Os was separated from Re and the PGEs using a $CHCl_3$/HBr liquid extraction procedure (modified after Cohen and Waters, 1996). Osmium was further purified using an H_2SO_4/H_2CrO_4 microdistillation technique (Birck et al., 1997). After Os extraction, Re and the PGEs were separated using a procedure adapted from the method of Pearson and Woodland (2000). Osmium was loaded as a bromide on Pt ribbon filaments covered with a $NaOH/Ba(OH)_2$ activator (Luguet et al., 2008). The $^{187}Os/^{188}Os$ isotope ratio and Os concentration measurements were carried out in negative mode using a Finnigan TRITON thermal ionization mass spectrometer (TIMS) at the Department of Lithospheric Research, University of Vienna, Austria. Isobaric interferences of ^{187}Re on ^{187}Os were monitored by measuring $^{185}ReO_3{}^{3-}$ (mass 233), and values were corrected for interferences. Mass fractionation was corrected offline using $^{192}Os/^{188}Os$ = 3.083 (Völkening et al., 1991; Luguet et al., 2008). The Os total procedural blank was ~0.8 pg. Highly siderophile elements were measured (Re and selected platinum-group elements) using a Thermo Element XR sector field–inductively coupled plasma–mass spectrometer (SF-ICP-MS) in single-collector mode at the Steinmann-Institute at the University of Bonn, Bonn, Germany, using methods described in Luguet et al. (2015). Total blanks for this study (*n* = 4) were ~4 pg for Re, ~3 pg for Ir, and ~22 pg for Pt. All reported concentration values were blank corrected.

Selenium and Tellurium Concentrations and Se Isotope Measurements

In order to simultaneously purify selenium (Se) and tellurium (Te) from a single sample digest, we followed the protocol

by Yierpan et al. (2018) and Kurzawa et al. (2019). This involves weighing sample material equivalent to ~30 ng Se (the exact Te amount is uncritical) into conventional Teflon beakers, adding adequate amounts of ^{74}Se-^{77}Se double-spike (1:1; sample Se:double spike Se) and ^{125}Te single spike (^{125}Te amount for estimated 3 ng sample Te, exact match uncritical; König et al., 2012), and digesting the sample-spike mixtures in an acid mixture of 5:1 (v/v) concentrated HF to concentrated HNO_3 in closed beakers on a hot plate at 85 °C for 48 h. Se and Te were purified from sample solutions by two-step ion-exchange chromatography. First, we employed an anion exchange column to remove Fe and collect purified Te. Second, Se was purified using a cation exchange column to remove remaining cations. Te concentrations were then determined by hydride generator quadrupole ICP-MS on an iCAP Qc instrument, and Se isotope abundances and elemental concentrations were measured by hydride generation multicollector ICP-MS on a ThermoFisher Scientific NeptunePlus instrument at the Isotope Geochemistry Laboratory, University of Tübingen, Tübingen, Germany. Typically, currents of 0.8–0.9 V were obtained on mass ^{82}Se during measurements (using an amplifier resistor of 10^{11} Ω) for a 30 ng/mL Se solution, with operating parameters similar to those reported by Kurzawa et al. (2017). A signal of 120,000 cps on mass ^{126}Te was obtained for a Te standard solution of 0.5 ng/mL, similar to operating parameters reported by Yierpan et al. (2018). Se and Te concentrations were determined at similar signal intensities compared to those of standard solutions.

Selenium isotope values are consistently expressed as $\delta^{82/76}Se$ (in ‰) relative to the NIST3149 reference material (e.g., Kurzawa et al., 2017) throughout this study. Measurements of the interlaboratory standard solution MH-495 relative to NIST3149 yielded an average value of $\delta^{82/76}Se$ of −3.25‰ ± 0.08‰ (2 standard deviation [s.d.], $n = 20$, 30 ng mL^{-1} solutions), indistinguishable from results of previous studies (Kurzawa et al., 2017; Yierpan et al., 2018, 2019). External reproducibility is conservatively expressed as 0.10‰ (2 s.d.), based on replicate digests and measurements of different samples and reference materials during multiple measurement sessions over 12 months (Yierpan et al., 2019, 2020). All samples were chemically processed and measured together with the international rock reference material USGS BCR-2, for which we obtained 76.9 ng g^{-1} Se, 2.51 ng g^{-1} Te, and $\delta^{82/76}Se_{NIST3149} = 0.29‰ ± 0.04‰$ (2 s.d.). These results are indistinguishable from values obtained previously (76 ± 1 ng g^{-1} Se, 2.54 ± 0.08 ng g^{-1} Te, and $\delta^{82/76}Se_{NIST3149} = 0.29‰ ± 0.05‰$, all $n = 5$; Yierpan et al., 2018). Long-term analytical reproducibility for both Se and Te concentration determinations is ~3% relative s.d. (1 s.d.; Yierpan et al., 2019, 2020). All blanks were below detection limit.

RESULTS

Major- and Trace-Element Analyses

Table 1A shows chemical data for the granophyre sample suite in this study. The compositions of sample BG-168, also analyzed in this study, and of other samples studied previously by Koeberl et al. (1996), are listed. Some first-order observations can be made based on these data:

(1) The main chemical differences between Dominion Group meta-lava and epidiorite are the slightly lower SiO_2 and Na_2O contents in Dominion Group meta-lava, and significantly higher Al_2O_3 in Dominion Group meta-lava (14.6 ± 0.7 wt% and 13.0 ± 0.8 wt% in epidiorite) and MgO contents in epidiorite (8.67 ± 1.01 wt%, compared with 6.09 ± 0.79 wt% in Dominion Group meta-lava).

(2) Felsic granophyre and mafic granophyre are, first of all, distinguished by SiO_2 content (felsic granophyre > 66 wt%, mafic granophyre < 66 wt%), average epidiorite (38 analyses) has 53.3 ± 0.4 wt% SiO_2. and Dominion Group meta-lava (16 analyses) has 54.2 ± 0.8 wt% SiO_2 (after Wannek, 2015). Felsic granophyre is characterized by elevated K_2O and lesser Fe_2O_3, MgO, CaO, and Na_2O than values measured for mafic granophyre (compare Table 1A).

(3) Only Cr and Sr contents seem to have a notable difference between the trace-element compositions of Dominion Group meta-lava and epidiorite. The distinction between the trace-element compositions of mafic granophyre and felsic granophyre is made by comparatively higher abundances of especially Sc and V, Co, Cu, and Zn in mafic granophyre, which are well on a trend with the even higher values in the mafic country rocks. Zn forms an exception in this regard. The trend, from high values in mafic country rock, via mafic granophyre, and then to the even lower values for felsic granophyre, is also consistent with the Rb, Zr, and Ba abundances. In contrast, the Cr and Sr contents cannot be explained simply by admixture of mafic country rock to felsic granophyre in order to form mafic granophyre. Both of these elements occur at very high abundances in both Dominion Group meta-lava and epidiorite.

(4) In contrast to the very limited range of Cr contents in felsic granophyre that had been reported previously (ranging from 419 to 428 ppm, data by instrumental neutron activation analysis [INAA]; Koeberl et al., 1996), our Cr data for mafic and felsic granophyre samples (obtained using ICP techniques; Table 1A) are markedly lower, ranging from 174 to 250 ppm. It should be noted that the Koeberl et al. (1996) study and the present one did not use the same sizes of sample aliquots; thus, a nugget effect with respect to the Cr carrier phase cannot be excluded. However, it is more likely that granophyre, in general, is characterized by widely fluctuating Cr contents. For example, Reimold et al. (1990) determined Cr abundances in granophyre by INAA between 85 and 261 ppm, and Therriault et al. (1997) reported values between 291 and 469 ppm from XRF analyses.

(5) All samples previously analyzed by Koeberl et al. (1996) were of the felsic granophyre type with SiO_2 contents >66 wt%.

TABLE 1A. SELECTED MAJOR- AND TRACE-ELEMENT ANALYSES FROM WANNEK (2015) FOR THE GRANOPHYRE,
DOMINION GROUP META-LAVA (DGL), AND EPIDIORITE SAMPLES USED IN THE PRESENT WORK

Sample	DW-26	Avg. DGL	DW-32	Avg. epid.	DW-9A	DW-33	DW-24	DW-17	DW-34
	DGL	n = 16	epidiorite	n = 38	MG	MG	MG	FG	FG
SiO_2	52.8	54.2 ± 0.9	50.6	53.3 ± 0.4	58.40	60.4	59.7	65.7	67.0
TiO_2	0.81	0.81 ± 0.08	0.79	0.66 ± 0.55	0.64	0.65	0.64	0.53	0.54
Al_2O_3	17.4	14.6 ± 0.7	14.7	13.0 ± 0.8	13.5	13.1	13.2	13.2	12.9
Fe_2O_3	9.25	11.4 ± 0.5	10.0	10.7 ± 0.45	10.4	10.3	9.95	7.4	7.33
MnO	0.17	0.18 ± 0.02	0.16	0.16 ± 0.01	0.15	0.17	0.15	0.15	0.15
MgO	5.59	6.04 ± 0.79	8.44	8.67 ± 1.16	4.63	4.49	4.35	3.58	3.65
CaO	12.1	10.8 ± 0.81	11.7	9.65 ± 0.59	6.79	6.04	6.41	4.06	4.01
Na_2O	1.03	1.47 ± 0.41	2.28	2.10 ± 0.28	2.85	2.65	2.86	2.46	2.40
K_2O	0.14	0.14 ± 0.03	0.29	0.53 ± 0.03	1.81	1.69	1.84	2.11	1.99
P_2O_5	0.20	0.17 ± 0.02	0.06	0.08 ± 0.01	0.10	0.12	0.11	0.10	0.10
L.O.I.	0.4	0.59 ± 0.14	1.0	1.25 ± 0.31	0.1	0.2	b.d.l.	0.4	b.d.l.
TOTAL	99.89		100.02		99.17	99.81	99.25	99.69	100.07
Sc	32		34		20	22	19	13	13
V	219		215		135	134	130	82	82
Cr	749		714		186	188	174	250	245
Co	52		46		33	31	29	23	21
Ni	310		226		105	100	99	104	105
Cu	161		121		67	66	65	55	55
Zn	79		69		74	79	71	55	58
Ga	20		14		16	16	16	15	15
Rb	7		8		54	57	58	62	62
Sr	459		234		210	211	210	223	229
Y	20		14		19	20	17	15	14
Zr	105		55		125	132	129	144	142
Ba	94		81		333	345	352	435	440
La	15		<10		25	28	28	33	25
Ce	40		10		54	57	51	56	57

Note: Major element data are in wt%, and trace element data are in ppm. Major-element analyses were conducted by X-ray fluorescence (XRF); trace-element analyses were conducted by inductively coupled plasma–mass spectroscopy (ICP-MS) and inductively coupled plasma–optical emission spectroscopy (ICP-OES). Average compositions calculated from 16 Dominion Group and 38 epidiorite analyses, together with 1σ standard deviations are also given (after Wannek, 2015). All Fe is given as Fe_2O_3. b.d.l.—below detection limit; L.O.I.—loss on ignition.

The major- and trace-element analyses of the VPU samples from the profile across the granophyre dike crossing Kopjeskraal farm are listed in Table 1B. The average epidiorite composition as given by Wannek (2015; average for 38 samples) is also listed. The elemental profiles of Figures 4A (major elements) and 4B (trace elements) extend from Archean granite gneiss (at the east end of the profile, sample VPU 06), across typical felsic grano-phyre (samples VPU 23 and 05, perhaps sample 07 as well, but here the MgO content is already slightly enhanced in compari-son to the other two samples, and silica reduced further than for samples 23 and 05), and into what Wannek (2015) had termed a "hybrid" phase and interpreted to result from the assimilation of epidiorite into felsic granophyre. This hybrid corresponds to our mafic granophyre. This profile extends roughly to the center of the dike, as indicated in Figure 2.

The elemental trends for this profile illustrate the gradual compositional change from felsic granophyre at contact with granitic country rock into the interior of the dike that is formed by mafic granophyre. This behavior is already obvious in the SiO_2 trend but particularly evident in the MgO and Fe_2O_3 trends. Calcium oxide indicates the same trend as well. Considering the composition of epidiorite DW-32 in Table 1A, and the average composition of epidiorite after Wannek (2015), the centermost hybrid (mafic granophyre, VPU 16) is, with respect to many major elements, still more "felsic" than the actual epidiorite (cf. e.g., SiO_2, MgO, and CaO abundances in Fig. 4A).

The trace-element trends of Figure 4B are rather variable. Where no clear trend from felsic granophyre to mafic granophyre is notable, this is, in part, due to significant sample-to-sample variabil-ity. Barium shows a somewhat erratic trend from felsic granophyre

TABLE 1B. MAJOR- AND TRACE-ELEMENT ABUNDANCES BY X-RAY FLUORESCENCE (XRF) FOR THE VPU PROFILE ACROSS THE GRANOPHYRE DIKE AT KOPJESKRAAL

Sample	VPU 16	VPU 15	VPU 14	VPU 13	VPU 12	VPU 11	VPU 10	VPU 09	VPU 08	VPU 07	VPU 05	VPU 23	VPU 06	Average ± 1σ
	MG	MG	MG	MG	MG	MG	MG	MG	MG	FG	FG	FG	granite	epidiorite
SiO_2	60.6	63.4	60.6	59.8	60.5	63.4	65.6	65.4	65.4	66.3	67.4	68.3	71.9	53.3 ± 0.4
TiO_2	0.68	0.57	0.67	0.68	0.62	0.60	0.48	0.49	0.55	0.53	0.52	0.52	0.27	0.60 ± 0.05
Al_2O_3	13.5	13.0	13.4	13.4	13.4	13.3	13.0	13.0	13.0	12.5	12.8	12.7	14.6	13.0 ± 0.8
Fe_2O_3	9.82	8.11	9.80	10.10	9.29	8.40	7.37	7.36	7.45	7.34	7.40	6.98	1.65	10.7 ± 0.45
MnO	0.16	0.15	0.16	0.16	0.18	0.15	0.15	0.16	0.15	0.14	0.14	0.13	0.02	0.16 ± 0.01
MgO	4.06	3.82	4.11	4.42	4.75	3.84	3.81	3.89	3.70	3.56	3.46	3.39	0.36	8.67 ±1.16
CaO	5.97	4.84	5.92	6.18	6.20	5.11	4.19	4.24	4.36	4.09	3.79	3.74	1.28	9.65 ± 0.59
Na_2O	2.76	2.57	2.77	2.71	2.62	2.66	2.52	2.58	2.54	2.43	2.31	2.33	3.87	2.10 ±0.28
K_2O	1.84	1.99	1.85	1.72	1.80	2.00	2.22	2.23	2.10	2.16	1.98	2.03	4.62	0.53 ± 0.09
P_2O_5	0.11	0.10	0.11	0.11	0.11	0.10	0.08	0.08	0.10	0.09	0.09	0.09	0.05	0.08 ± 0.01
L.O.I.	0.1	0.9	0.1	0.1	0.3	0.1	0.1	0.3	0.2	0.1	<0.1	<0.1	0.7	1.25 ± 0.31
TOTAL	99.60	99.45	99.49	99.38	99.77	99.66	99.52	99.73	99.55	99.24	99.89	100.21	99.32	

Note: Major-element data are in wt%, and trace element abundances are in ppm. Also given is an average epidiorite composition from Wannek (2015), based on 38 individual analyses for major elements and three analyses for trace elements; with 1σ standard deviations. MG—mafic granophyre, FG—felsic granophyre, L.O.I.—loss on ignition.

to mafic granophyre but with an overall significant decrease of abundances across the mafic granophyre field. Strontium and Rb abundances do not show significant changes along the granophyre. The Cr trend is characterized by strong sample-to-sample fluctuation and does not display any regular trend from felsic granophyre into mafic granophyre. The same holds for Zr, which is strongly enriched in the granite end member, in comparison to the possible epidiorite component. On average, mafic granophyre is slightly depleted over felsic granophyre in Ce. Lathanum and Y do not show significant trends. Clearly, V is relatively enriched in the mafic granophyre. The Ni abundances are somewhat erratic and, at best, display a marginal increase of values in the mafic granophyre zone. Zinc, Cu, and Co, in contrast, are distinctly enriched in mafic granophyre when compared to felsic granophyre.

Platinum Group Elements and Re-Os Systematics

The concentrations of selected PGEs (Os, Ir, and Pt) and Re of two mafic target rocks from the Vredefort area (Dominion Group meta-lava and epidiorite) and six granophyre samples are listed in Table 2, together with Re-Os literature data for four target rock samples (Witwatersrand shale and Ventersdorp lava) and data for six felsic granophyre samples (Koeberl et al., 1996). Witwatersrand shale and Ventersdorp samples were analyzed by Koeberl et al. (1996) as the likely carriers of target rock PGE components. The Re and Os concentration and $^{187}Os/^{188}Os$ isotope data presented in this work include a replicate measurement of sample BG-168, previously analyzed by Koeberl et al. (1996). Although comparable, the different analyses reflect a minor inhomogeneity, which is likely due to the nugget effect and, probably, different masses of bulk powder used in the two independent studies.

Rhenium and Os concentrations of samples from this study vary from 148 to 879 ppt for Re and from 45 to 103 ppt for Os. Ir and Pt concentrations range from 24 to 113 ppt and from 354 to 2966 ppt, respectively. Corresponding interelement ratios vary from 0.90 to 1.88 for Os/Ir and from ~15 to ~44 for Pt/Ir. These ratios roughly agree with typical upper continental crustal (UCC) values of ~1.4 and 32.7, respectively (Peucker-Ehrenbrink and Jahn, 2001), and, in the case of the Pt/Ir ratios, they are significantly outside the range for chondrites (carbonaceous chondrites exhibit Os/Ir ratios of ~1.1 and Pt/Ir ratios of ~2.0; e.g., Tagle and Berlin, 2008). Figure 5 shows UCC-normalized PGE patterns for all analyzed samples, showing the different fractionation patterns of granophyre samples compared to those for the epidiorite and Dominion Group meta-lava samples.

Dominion Group meta-lava and epidiorite have very different abundance patterns, particularly for Ir and Pt, and both are different from mafic granophyre and felsic granophyre. Felsic granophyre shows a large range of PGE abundances, and all three mafic granophyre samples plot between two of the felsic granophyre samples and the epidiorite patterns. The third felsic granophyre sample has a pattern that is indistinguishable from mafic granophyre patterns.
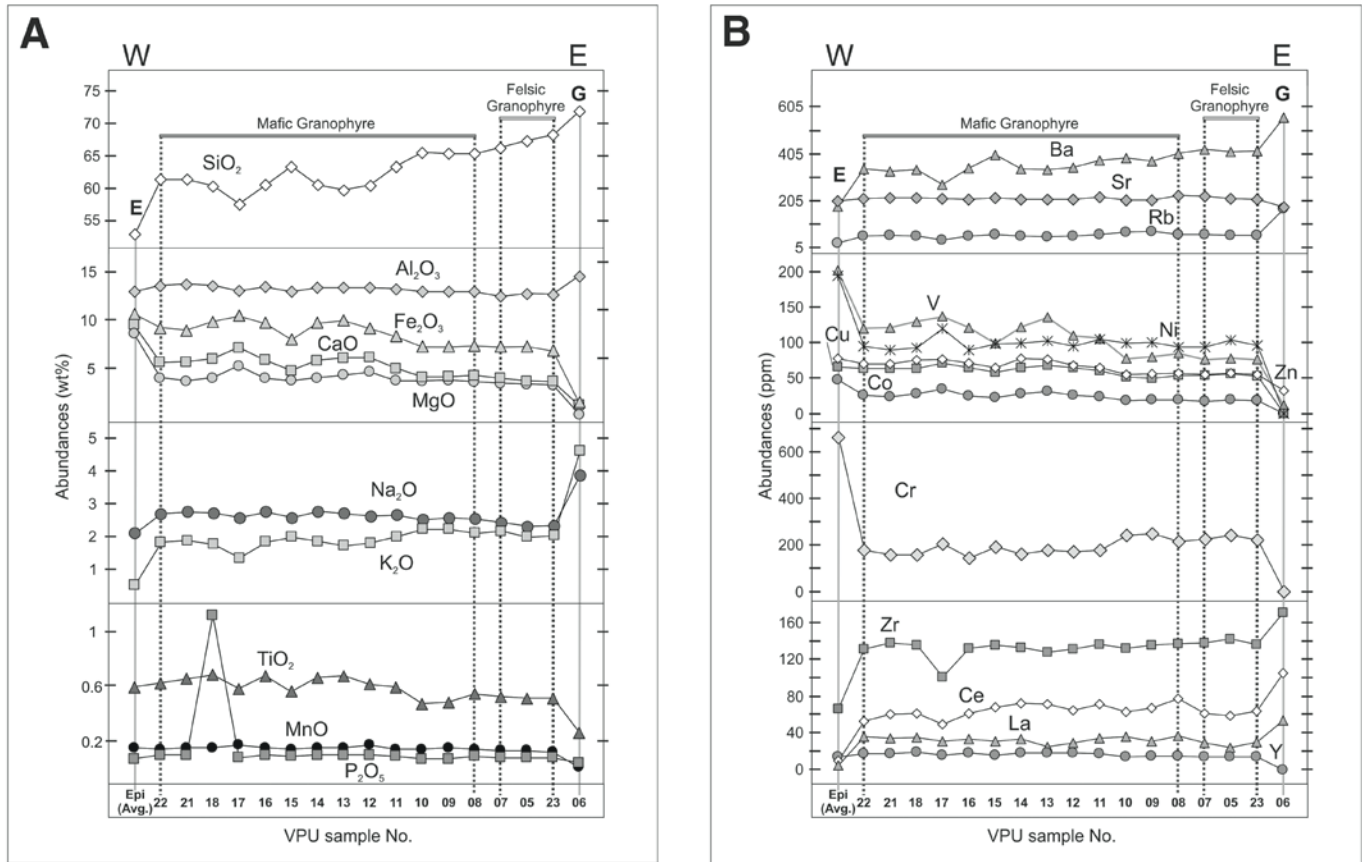
Figure 4. (A) Major-element profiles across the sampled NE-SW section of the granophyre dike at Kopjeskraal. The VPU samples (Table 1B) were obtained from granite (G) at the eastern contact with granophyre and then toward the inner part of the dike. Samples were taken at more or less regular intervals of 2 m. An epidiorite (E) analysis is plotted, for comparison, on the western side of the profile, and the average major-element abundances for the average epidiorite composition of Wannek (2015; given here in Table 1B) have also been plotted for E. (B) Profiles for abundances of selected trace elements for the VPU sample suite. Details are the same as for A.

The $^{187}Os/^{188}Os$ isotope ratios for the two analyzed mafic target rocks span a range from slightly subcrustal values (UCC = 1.05 ± 0.23; Peucker-Ehrenbrink and Jahn, 2001) for the Dominion Group meta-lava up to highly radiogenic signatures of around 9.4 (epidiorite). These values are within the range for the, mostly UCC-like, target lithologies (Witwatersrand shale and Ventersdorp lava) previously analyzed by Koeberl et al. (1996). These authors reported $^{187}Os/^{188}Os$ isotope ratios up to ~6.27. Most granophyre samples mirror typical values for UCC. The only exceptions are (1) two of the analyzed mafic granophyre samples, which exhibit values intermediate between UCC and epidiorite, and (2) the felsic granophyre samples analyzed by Koeberl et al. (1996), which were postulated to contain a meteoritic admixture. The latter have values between meteoritic signatures (~0.12; e.g., Shirey and Walker, 1998) and UCC.

The $^{187}Re/^{188}Os$ ratios of epidiorite and Dominion Group meta-lava are ~68.7 and ~15.6, respectively. These values are comparable to those of the granophyre samples analyzed in this study (ranging from ~17.6 to ~93.3) and overlap with the range

for granophyre previously determined by Koeberl et al. (1996). The average value for UCC is, for comparison, ~34.5 (Peucker-Ehrenbrink et al., 2001). The $^{187}Re/^{188}Os$ ratios reported by Koeberl et al. (1996) for felsic granophyre samples are significantly lower (close to the chondritic value of ~0.39; Shirey and Walker, 1998) compared to values from our study. However, Koeberl et al. (1996) also reported $^{187}Re/^{188}Os$ ratios up to 1153 for shales from the Vredefort region.

Figure 6A shows all Re-Os isotope data so far obtained for target rocks and impactites from the Vredefort region. As mentioned above, Dominion Group lava and epidiorite have distinctly different Re-Os isotopic characteristics. The Dominion Group meta-lava sample plots into the granophyre field of Koeberl et al. (1996), whereas the epidiorite has comparatively radiogenic $^{188}Os/^{187}Os$ and high $^{188}Re/^{187}Os$ ratios. Notably, the Ventersdorp lava sample from Koeberl et al. (1996) plots distinctly different from epidiorite, which is obviously not in keeping with the long-discussed possible relationship between epidiorite sills in the Vredefort collar and a feeder dike system for

TABLE 2. ABUNDANCES OF Re AND SELECTED PLATINUM GROUP ELEMENTS (Os, Ir, AND Pt) AND
Re-Os ISOTOPE COMPOSITIONS FOR VREDEFORT GRANOPHYRE AND COUNTRY ROCK SAMPLES FROM THIS STUDY

Lithology	Sample	Re (ppt)	Os (ppt)	Ir (ppt)	Pt (ppt)	$^{187}Re/^{188}Os$	$^{187}Os/^{188}Os$
This study							
Dominion Group lava	WUR DW 26	148	48	50	1954	15.61 (46)	0.6033 (18)
Epidiorite	WUR DW 32	293	45	24	354	68.66 (87)	9.434 (20)
Mafic granophyre	WUR DW D9A	704	45	50	1812	82.46 (97)	0.9343 (73)
Mafic granophyre	WUR DW 33	648	54	54	2089	93.25 (89)	4.890 (19)
Mafic granophyre	WUR DW 24	674	73	39	1695	61.79 (75)	3.1766 (60)
Felsic granophyre	WUR DW 17	230	70	74	2966	17.62 (53)	1.0191 (54)
Felsic granophyre	WUR DW 34	655	59	38	1650	59.39 (78)	1.0513 (46)
Felsic granophyre	BG-168	879	103	113	2610	43.47 (88)	0.6585 (13)
Koeberl et al. (1996)							
Felsic granophyre	BG-168	750	162	–	–	23.87	0.668 (2)
Felsic granophyre	BG-4/1	289	1110	–	–	1.262	0.196 (1)
Felsic granophyre	BG-4/2	256	356	–	–	3.557	0.286 (2)
Felsic granophyre	BG-7/2	266	111	–	–	12.22	0.558 (2)
Felsic granophyre	BG-9	255	228	–	–	5.611	0.410 (2)
Felsic granophyre	BG-10	256	131	–	–	9.875	0.458 (2)
Shale	S1/1	5060	53	–	–	536.0	1.240 (4)
Shale	S1/2	7316	37	–	–	1153	1.572 (4)
Shale	SNE	184	162	–	–	6.09	1.013 (3)
Ventersdorp lava	UP-63	9866	16	–	–	5418	6.272 (20)

Note: Data are from this study and from the literature (Koeberl et al., 1996). Iridium and Pt data were not reported in Koeberl et al. (1996). This table also shows literature Re and Os concentrations, as well as Re-Os isotopic compositions for target rocks and meteorite-contaminated felsic granophyre (FG) samples from Koeberl et al. (1996). Analysis of sample BG-168 was from the same bulk powder as in Koeberl et al. (1996).
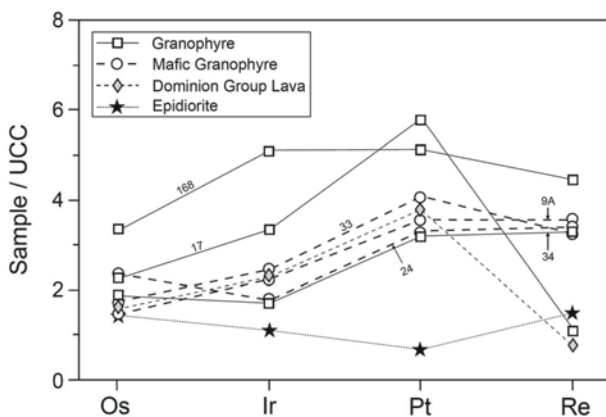

Figure 5. Platinum group element (PGE) patterns (plus Re) of felsic and mafic granophyre (FG and MG, respectively), Dominion Group Lava (DGL), and epidiorite samples. Data were normalized to upper continental crust (UCC; Palme and O'Neill, 2003). See text for discussion.

regional Ventersdorp extrusion (as suggested, e.g., by Pybus, 1995; Reimold et al., 2000).

Selenium-Tellurium Concentrations and Se Isotope Data

Results for Se-Te concentrations and Se isotopes are listed in Table 3. Concentrations of Se and Te concentrations in the analyzed target rocks range from 146 to 152 ppb for Se and from 2.43 to 3.24 ppb for Te in the epidiorite and Dominion Group meta-lava, respectively (corresponding Se/Te are ~47 and ~60). Elemental abundances range from 47.8 to 51.8 ppb Se and from 1.70 to 1.88 ppb Te in felsic granophyre and from 114 to 123 ppb Se and from 3.26 to 3.93 ppb Te in mafic granophyre. In contrast to the target rocks, corresponding Se/Te are rather uniform for granophyre, ranging from ~30 to ~35, except for felsic granophyre sample BG-168, which exhibits a slightly lower ratio of 25.4. Interestingly, these elemental Se-Te systematics are within the range of peridotite values (König et al., 2014, 2015).

The first $\delta^{82/76}Se$ values determined for target rocks vary from −1.32‰ (epidiorite) to −0.31‰ (Dominion Group meta-lava), and granophyre samples range from −0.29‰ to 0.37‰ (all ±0.1‰, 2 s.d.). The epidiorite isotope value is the lowest but lies
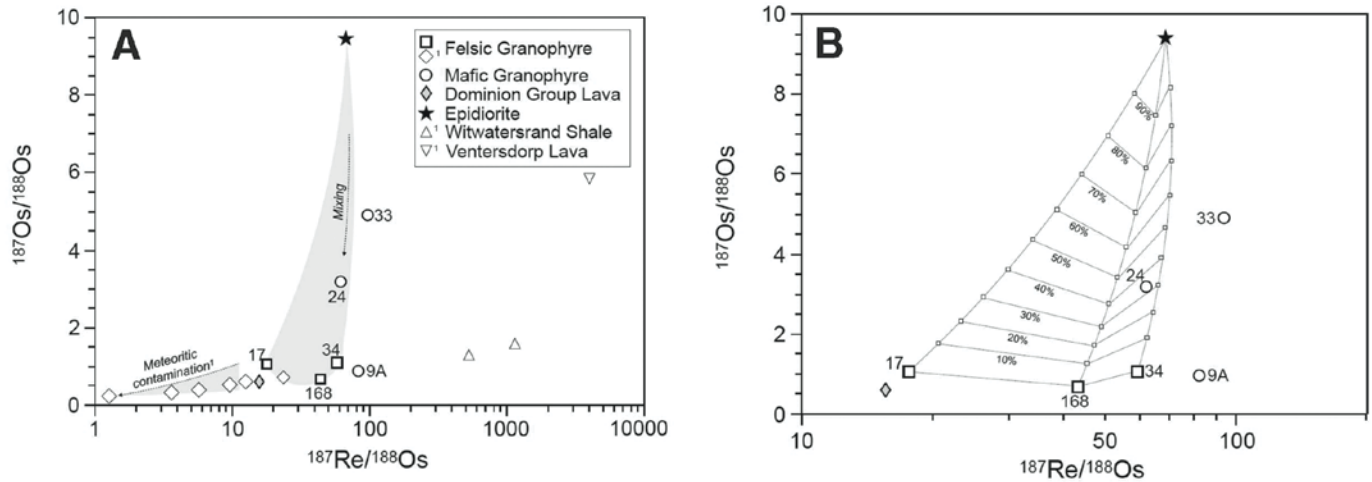
Figure 6. (A) $^{187}Os/^{188}Os$ vs. $^{187}Re/^{188}Os$ diagram showing all available Re-Os isotope data for Vredefort impactites and target rocks from the literature and data from this study. A postulated trend for meteoritic admixture (Koeberl et al., 1996) is superimposed as a gray shaded area. Data from Koeberl et al. (1996) are marked in the legend with a superscript ([1]). All felsic granophyre samples analyzed in this study plot off this trend. Instead, felsic granophyre samples from this study, together with the epidiorite, define a mixing trend generating the mafic granophyre. (B) $^{187}Os/^{188}Os$ vs. $^{187}Re/^{188}Os$ isotope diagram, showing the calculated mixing proportions of epidioritic component to felsic granophyre that would generate mafic granophyre. Notably, Dominion Group lava plots clearly outside the mixing field.

at the lower end of all reported terrestrial samples (~−3.0‰ to +3.0‰; see Stüeken, 2017) and well within the range of values reported for reduced Se-bearing sulfide (−4.48‰ to −0.39‰; König et al., 2019). A recent duplication of the analysis of the epidiorite DW-32 yielded confirmation of this very low isotope ratio: the repeat value and error (−1.25 ± 0.09) are very similar, within error limits, to the original values (−1.32 ± 0.06; cf. Table 3). All other analyzed samples fall into a ten-times narrower range, more comparable to terrestrial mantle values defined by mid-ocean-ridge basalt (MORB) and peridotites ($\delta^{82}/^{76}Se$ ranging from −0.30‰ to 0.10‰; Yierpan et al., 2019; Varas-Reus et al., 2019) as well as chondrites (Labidi et al., 2018).

DISCUSSION

Major- and Trace-Element Composition

The target for the Vredefort impact event consisted of a succession of Archean granitoid basement overlain successively by the Witwatersrand Supergroup, dominated by arenitic and argillitic lithologies, the Ventersdorp Supergroup, in general basaltic/andesitic intrusive and extrusive lithologies, and, finally, the Transvaal Supergroup carbonate, with some arenitic rocks (e.g., Gibson and Reimold, 2008; Gibson, 2019). In the past, target lithologies that were considered major contributors

TABLE 3. SELENIUM AND TELLURIUM ABUNDANCES AND Se ISOTOPE COMPOSITIONS OF
VREDEFORT TARGET ROCKS AND GRANOPHYRE

Lithology	Sample	Se (ppb)	Te (ppb)	Se/Te	$\delta^{82}/^{76}Se$
Dominion Group lava	WUR DW 26	148	2.43	60.2	−0.305 ± 0.054
Epidiorite	WUR DW 32	152	3.24	46.8	−1.316 ± 0.060
Mafic granophyre	WUR DW D9A	122	3.93	31.1	0.268 ± 0.065
Mafic granophyre	WUR DW 33	123	3.53	34.8	0.121 ± 0.060
Mafic granophyre	WUR DW 24	114	3.26	35.1	−0.292 ± 0.040
Felsic granophyre	WUR DW 17	51.8	1.70	30.5	0.067 ± 0.075
Felsic granophyre	BG-168	47.8	1.88	25.4	0.373 ± 0.060
STD this study	BCR-2	76.9	2.51	30.7	0.287 ± 0.043
STD literature	BCR-2	76 ± 1	2.54 ± 0.08	28.6–31.3	0.29 ± 0.05

Note: Data for U.S. Geological Survey reference material STD BCR-2 from this study in comparison to literature values (average of *n* = 5; Yierpan et al., 2018) are also shown. Internal errors in % (±2σ) on single measurements are always better than external reproducibility of 0.1% (±2σ). See text for details.

to the Vredefort granophyre mixture were thought to be Archean granite gneiss, Witwatersrand quartzite, and Witwatersrand shale (Reimold et al., 1990), all of which are prominent in the clast populations of granophyre. Other workers, such as French et al. (1989) and French and Nielsen (1990), also considered Ventersdorp Supergroup lava as a possible mafic precursor unit.

Since the recognition of a distinct mafic granophyre phase in the last decade, it has been important to search for evidence to support either general or only local contributions of mafic precursor to granophyre impact melt. A general contribution to bulk impact melt rock would mean that both felsic granophyre and mafic granophyre could contain a mafic precursor component, whereas local assimilation of a Ventersdorp Supergroup component (i.e., epidiorite) has been advocated by several previous granophyre workers (for a recent review, see, e.g., Reimold et al., 2017). Wannek (2015) and Reimold et al. (2017) proposed that mafic granophyre on the Kopjeskraal property was formed by local assimilation (admixture) of an epidiorite type component during dike emplacement. In this context, two major research questions are being investigated here:

(1) Is there general evidence for a mafic contribution to granophyre?
(2) Are there further clues to be gained from the present isotope analysis regarding the formation of mafic granophyre?

Based on conventional isotope (i.e., Sr-Nd-Pb) analysis, Reimold et al. (2017) concluded that mafic granophyre had a distinctly stronger affinity to epidiorite than to Dominion Group meta-lava. Considering the respective chemical compositions for the mafic country rocks and the two varieties of felsic and mafic granophyre, as laid out in detail here, mafic granophyre can be considered a phase that is intermediate in composition to the mafic country rocks and felsic granophyre. This is particularly based on SiO_2, TiO_2, MgO, and CaO abundances (see, e.g., Fig. 4A). It is obvious from this figure that this trend is not maintained for Fe, Na, and K oxides; to explain the behavior of these elements, other country rock types must be invoked. The shale component shown by the mixing calculations of Reimold et al. (1990) to be involved in the formation of felsic granophyre at a significant proportion (9–14 rel%) is characterized by up to >30 wt% Fe_2O_3 (Reimold et al., 1990, their table 2c). The main protolith phase, the Archean granite gneiss of the crystalline basement, must be considered as a major source of alkali elements in the granophyre. The mafic country rocks, epidiorite and Dominion Group meta-lava, have strongly elevated CaO contents compared to values for the mafic granophyre. A first-order balance calculation for CaO and MgO in epidiorite and felsic granophyre results in a significant contribution of epidiorite to felsic granophyre in order to generate mafic granophyre.

In terms of trace-element abundances, it was noted above that several mixing trends between felsic granophyre and epidiorite are indicated in Figure 4B, for Ba, V, possibly Ni, weakly for Ce, and notably for Zn, Cu, and Co. Several trace-element distribution patterns for VPU samples are marred by strong sample-to-sample variability. Such is the case for Cr, for which not only admixture (assimilation) of an epidiorite component to felsic granophyre must be considered, but also possible variability in the shale component. The West Rand shales of the Witwatersrand Supergroup, in part, are characterized by high Cr abundances (e.g., French et al., 1989). Discrepancies in Cr abundances are noted between the data for felsic granophyre presented by Koeberl et al. (1996) and Reimold et al. (1990), and that for mafic granophyre and felsic granophyre listed here in Table 1A. Further discrepancies are inherent to the compilations of granophyre analyses by Reimold and Gibson (2006) and Therriault et al. (1997), who did not distinguish between mafic granophyre and felsic granophyre compositions. This is also the case for the wide spread of Cr abundances for mafic granophyre and felsic granophyre, respectively, obtained by Wannek (2015). Chromium analysis by XRF spectrometry is no simple feat and may require separate calibration curves for relatively low (<300 ppm) and relatively high (>300 ppm) abundance ranges. On the other hand, the small sample sizes applied in INAA could lead to nugget effects. Overall, there is evidence in the trace-element data for admixture of epidiorite end-member component to felsic granophyre, as was also demonstrated for the major-element data. The fluctuations noted for several of the patterns may be explained by the varied proportions at which epidiorite was mixed in, by heterogeneous distribution of certain elements, such as Cr, across the granophyre dike, and/or by analytical problems (again, for instance, in the case of Cr).

Based on the average chemical compositions for Dominion Group meta-lava and epidiorite, as given in Table 1A, most major elements have overlapping abundance ranges for these lithologies. As already discussed above, the relatively higher MgO and CaO contents of epidiorite favor the interpretation that a significant contribution from epidiorite could have been incorporated into felsic granophyre toward the generation of mafic granophyre. The selected Dominion Group meta-lava and epidiorite trace-element analyses in Table 1A do not allow us to discriminate between possible contributions to felsic granophyre from these respective lithologies at this time.

Platinum Group Element Abundances and Re-Os Systematics

Compared to the previous results for felsic granophyre samples (Koeberl et al., 1996), our new granophyre analyses (including both the felsic and the mafic varieties) have much lower Os contents and higher $^{187}Re/^{187}Os$ ratios. As shown in Figure 6A, none of the granophyre samples analyzed in this study plots on the trend defining a meteoritic admixture. Instead, our data separate the $^{187}Re/^{187}Os$ isotope ratios for our granophyre samples further from the meteorite data field. Clearly, the new samples from Kopjeskraal give no indication for the presence of a meteoritic component, in contrast to the former suite of samples analyzed by Koeberl et al. (1996). This is likely due to heterogeneous admixture of the meteoritic component to impact melt, as already

surmised by Koeberl et al. (1996). Thus, extraterrestrial contamination of granophyre, according to the extended Re-Os isotope data set presented in this study, affected only part of the lithology and probably none of the mafic granophyre samples.

Instead, mafic granophyre samples lie on a mixing trend between epidiorite and felsic granophyre (Fig. 6A). Such a mixing relationship is supported by major- and trace-element data (as discussed above) and PGE patterns plus Re patterns as shown in Figure 5 (all mafic granophyre samples plot between the PGE pattern of felsic granophyre, samples 168 and 17, and epidiorite; see Results section). From all these trends, it can be considered that the mafic (epidiorite) component would not have been admixed to felsic granophyre melt at a constant proportion. In an attempt to approximate the amount of mafic admixture to the felsic granophyre lithology necessary to produce the mafic granophyre composition (via assimilation), we calculated mixing trends in the $^{187}Os/^{188}Os$ versus $^{187}Re/^{188}Os$ diagram, which are shown in Figure 6B. Notably, ~35%–40% admixture of an epidioritic component to felsic granophyre could produce mafic granophyre sample 24, and an ~55%–60% admixture could produce mafic granophyre sample 33. However, sample 33 plots somewhat outside of the mixing field. We attribute this to the fact that the epidiorite component admixed to the felsic granophyre lithology is not fully represented by the one epidiorite sample that has so far been analyzed in this study for Re and Os isotope abundances. The epidiorite lithology could well be characterized by chemical inhomogeneity.

In addition, the rather moderate Re content and Re/Os ratio of the analyzed epidiorite sample is not fully consistent with its highly radiogenic $^{187}Os/^{188}Os$ signature (which could only be achieved by considerable radiogenic ingrowth over time). Secondary mobilization of Re (i.e., loss of Re) during metamorphism could also have changed the Re/Os ratio to a lower value. On the other hand, the "real" felsic granophyre component may be well represented by the three felsic granophyre samples analyzed in this study. However, the arguments raised above explain the non-ideal mixing behavior shown in Figure 6B and other plots, which will be discussed below. This also clearly highlights the objectives for further studies on this topic. Notably, a $^{187}Os/^{188}Os$ versus Os plot, as shown in Figure 7A, also supports an ~40% admixture of epidioritic component to mafic granophyre sample 24 and an ~55% admixture of epidioritic component to sample 33, strengthening our mixing hypothesis. These findings also support the earlier conclusion of Reimold et al. (2017), who stated that admixture of epidiorite into superheated impact melt, followed by melting and assimilation, could have caused the generation of the mafic impact melt phase sampled at Kopjeskraal. The present results, combined with the findings of Reimold et al. (2017), and also Kovaleva et al. (2018, 2019), challenge the idea of Lieger (2011) and Lieger and Riller (2012) that successive pulses of differentiated impact melt caused the formation of composite mafic and felsic granophyre.

Selenium-Tellurium Concentrations and Se Isotope Data

The Se-Te concentrations obtained in this study can be readily interpreted in accordance with a mixing relationship between felsic granophyre and epidiorite, as favored by the major- and trace-element data and the Os isotope data discussed in the preceding section. The felsic granophyre samples exhibit lower Se and Te concentrations and lower Se/Te than the mafic granophyre samples. These, in turn, have slightly lower values compared to the Dominion Group meta-lava and epidiorite samples (Table 3). Figure 7B visualizes these relationships in the Se versus Se/Te diagram. Hypothetical mixing lines exemplify mafic granophyre generation via epidioritic contamination of a felsic granophyre magma rather than Dominion Group lava, which would otherwise result in higher Se/Te of the mixture than currently observed. Interestingly, mafic granophyre sample D9A perfectly plots between the epidiorite and the felsic granophyre fields in the Se-Te diagram (cf. Figs. 7A and 7B), although it plots outside most of the Re-Os–based mixing arrays. Thus, the Se-Te data also support the mixing/assimilation scenario for this sample.

A further assessment of the mixing relationship between the end-member lithologies can be attempted by combining the sensitive Re-Os isotope system with the novel Se-Te and Se isotope tool. Notably, Figures 7C and 7D (showing $^{187}Os/^{188}Os$ vs. Se/Te and $\delta^{82}/^{76}Se$) agree with our stated conclusions. Although the mixing fields would be significantly larger, taking into account a slight variability in the end-member composition (as indicated in Fig. 7B), mafic granophyre samples plot on or near the calculated mixing lines representing around 40% of an epidiorite component for sample 24 and around 60%–70% for sample 33 (thus agreeing with an average of 60% admixture, calculated based solely on Re-Os data). At this point in time, and on the basis of still-limited Re-Os isotope and Se-Te geochemical data, we must emphasize that these percent admixture values are tentative; however, the new results presented in this study consistently indicate a significant epidiorite admixture to felsic granophyre.

Moreover, the mixing relationships for $^{87}Os/^{188}Os$, $\delta^{82}/^{76}Se$, and Se/Te rule out a mixture of felsic granophyre with Dominion Group meta-lava (Figs. 7C and 7D). Hence, we suggest that the first Se isotope and Se-Te concentration data for Vredefort target rocks and impactites presented here support the implications from the more conventionally used Re-Os systematics and PGE concentrations. We suggest further potential to combine these tools exists for similar studies related to petrogenesis of impact-generated rocks. To exploit this potential, further studies are required to increase the limited Se isotope database on potential target rocks, in general, and Vredefort rocks, in particular.

CONCLUSIONS

New geochemical data for the mafic granophyre and felsic granophyre impact melt rock phases of the Vredefort impact structure, including major- and trace-element abundances (including Se-Te and PGE concentrations derived from isotope

dilution analysis), Re-Os systematics, and Se isotope data, were used to examine the hypothesis that mafic granophyre was generated by admixture-melting-assimilation of a mafic country rock type (likely epidiorite) to felsic granophyre. Our new chemical analyses of felsic granophyre and mafic granophyre, as well as of epidiorite and Dominion Group meta-lava, are consistent with our hypothesis. This is demonstrated by the following observations:

(1) Major-element data for the VPU traverse across a significant section of the granophyre dike on the Kopjeskraal property, comparing CaO and MgO abundances in the various analyzed lithotypes, indicates a significant epidiorite admixture to felsic granophyre to generate mafic granophyre, which is also consistent with the PGE patterns presented in this study.

(2) In an attempt to quantify the postulated epidiorite contribution to the felsic granophyre (to generate mafic granophyre), we performed mixing calculations based on Re-Os elemental and isotope data, which are ideally suited to detect mafic (and meteoritic) admixtures. Our data clearly indicate a lack of any meteoritic component for the analyzed felsic granophyre.
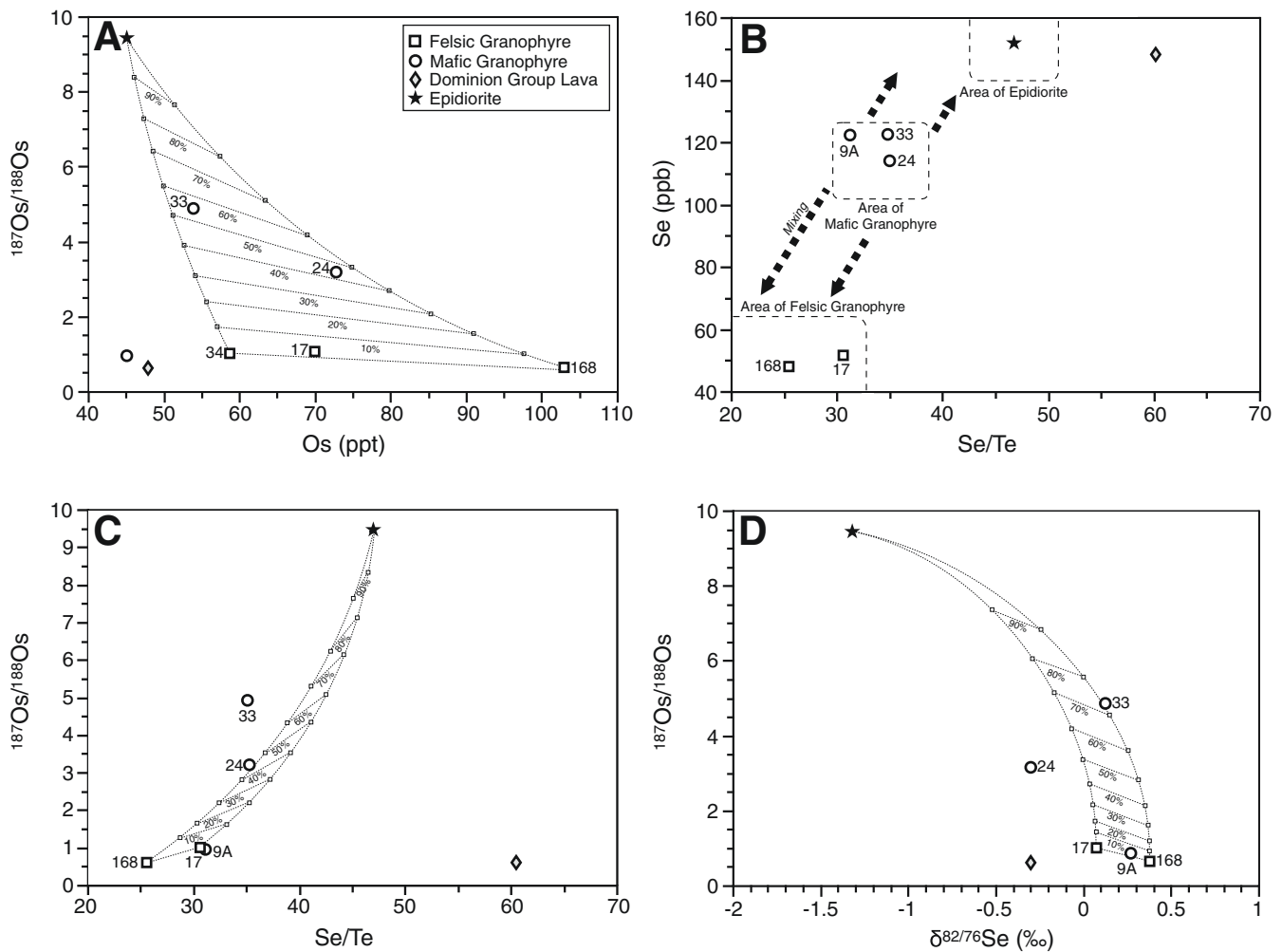
Figure 7. (A) ^{187}Os/^{188}Os vs. Os diagram showing felsic granophyre, mafic granophyre, epidiorite, and Dominion Group meta-lava analyzed in this study. Two of the three mafic granophyre samples (24 and 33) can be interpreted to result from admixture of about ~40% to ~60% of epidiorite component to the felsic granophyre (see text for discussion). (B) Selenium vs. Se/Te ratios for felsic granophyre, mafic granophyre, epidiorite, and Dominion Group meta-lava. Again, Dominion Group meta-lava samples plot (far) outside the postulated mixing trend between felsic granophyre and epidiorite (arrows). As the analyzed felsic granophyre, mafic granophyre, and especially epidiorite sample may not be fully representative of the full compositional diversity, we also show possible compositional areas for the different lithologies (felsic granophyre, mafic granophyre, and epidiorite). (C) ^{187}Os/^{188}Os vs. Se/Te diagram showing felsic granophyre, mafic granophyre, epidiorite, and Dominion Group meta-lava analyzed in this study. Mixing calculations confirm estimated values based solely on Re-Os data. Again, Dominion Group meta-lava plots clearly outside the mixing trend. (D) ^{187}Os/^{188}Os vs. $\delta^{82/76}$Se values for the samples analyzed. The mixing trend confirms conclusions based on other correlation diagrams. Errors for ^{187}Os/^{188}Os ratios are smaller than symbol sizes.

(3) Mixing calculations indicate varied proportions of epidio-rite admixture to felsic granophyre (via mixing or assimilation) of 40%–60%, resulting in mafic granophyre.

(4) Our Se and Te elemental and Se isotope data are also consistent with the postulated mixing trend. Coupled Re-Os, Se/Te, and Se isotope data, as presented in this study for the first time, consistently replicate mixing proportions calculated based solely on Re-Os isotope data.

(5) All lines of analytical evidence discussed here support the interpretation that the locally occurring mafic granophyre variety of the NW Vredefort Dome is the likely result of mixing between a felsic granophyre end member and a mafic country rock type, most likely epidiorite.

(6) Consequently, and as found in the previous conventional Sr-Nd-Pb isotope study (Reimold et al., 2017), our chemical data and Re-Os isotope results do not support a two-stage impact melt emplacement to account for the chemical and isotopic systematics of felsic and mafic granophyre at Kopjeskraal.

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