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Geochemistry (Isotope Geochemistry)

Tracing the emerald origin by oxygen isotope data: the case of Sandawana, Zimbabwe

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Abstract

Given the wide range of oxygen isotopic composition of emerald from all over the world ($\delta^{18}\text{O}$ between +6.2 and +24.7‰), the $\delta^{18}\text{O}_{\text{V-SMOW}}$ values of emeralds from the Sandawana mines in Zimbabwe ($\delta^{18}\text{O}_{\text{‰}} = +6.6$ to +8.0), are relatively constant, among the lowest ever measured. These consistently low values can be explained by host-rock buffering in a very narrow emerald-bearing reaction zone between ultrabasic greenstones (metamorphosed komatiites) and albitised pegmatites. $\delta^{18}\text{O}$ values of Sandawana emeralds overlap those of emeralds from Brazil, Austria, Australia and Madagascar, a fact indicating that, in these cases, oxygen isotope composition alone is not sufficient to determine the geographic origin of commercially available emeralds. However, stones with overlapping $\delta^{18}\text{O}$ values may eventually be identified using a combination of physical properties, inclusion characteristics and chemical composition. **To cite this article: J.C. Zwaan et al., C. R. Geoscience 336 (2004).**

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Résumé

La composition isotopique de l'oxygène des émeraudes de Sandawana (Zimbabwe) est relativement uniforme et très basse, parmi les plus faibles valeurs des $\delta^{18}\text{O}$ mesurées (+7,3 ± 0,7‰, pour une gamme de variation totale entre +6,2‰ et +24,7‰). Ces valeurs sont liées aux conditions de gisement, dans une étroite zone réactionnelle entre roches ultrabasiques et pegmatites albitisées, et imposées par le protolithe (komatiites métamorphiques). Des compositions comparables se retrouvent dans d'autres gisements (Brésil, Autriche, Australie, Madagascar), ce qui montre que la composition isotopique de l'oxygène n'est pas, à elle seule, une preuve univoque de l'origine. Toutefois, à condition d'associer les autres critères d'identification (propriétés physiques, inclusions minérales et fluides, composition chimique, notamment éléments en trace), on montre qu'il est en général possible de lever les ambiguïtés et de retrouver l'origine des gemmes. **Pour citer cet article : J.C. Zwaan et al., C. R. Geoscience 336 (2004).**

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1. Introduction

Stable-oxygen-isotope analysis of emeralds was recently promoted as a way to establish the country of origin of cut emeralds that are sold on the commercial market [10,11]. In these studies, only two measurements were done on emeralds from Sandawana, Zimbabwe, which seemed to indicate relatively small variations in oxygen isotope composition. The present study presents additional data on precisely located emeralds from the Zeus underground mine, and the Orpheus mine in the Sandawana district. We have no doubt that oxygen isotope data bring useful elements to the knowledge of emerald origin. However, relying only on this technique can be ambiguous if different occurrences show overlapping values. In this respect, the emeralds from Sandawana will be used to test this method in comparison with the traditional, non-destructive techniques, such as measuring the physical properties, characterising the inclusions, and chemical analysis.

2. Geological setting of Sandawana emerald deposits

The Sandawana emerald mines are located in the Low Veld of Zimbabwe (coordinates: 20°55'S and 29°56'E), 65 km south of the village Mberengwa [29, 30]. The emeralds occur along the southern limb of the Mweza greenstone belt (MGB), located at the southern margin of the Archean Zimbabwe Craton, at the border with the Limpopo Mobile Belt (Fig. 1). Just south of the Sandawana area, a major tectonic break dated at about 2.6 Ga [19] exists between the Zimbabwe craton and the Northern Marginal Zone (NMZ) of the Limpopo belt.

The MGB consists of a succession of intensely deformed sedimentary and volcanic rocks, of which banded iron formations (BIF), phyllites and greenstones form the main rock types. Especially at the southern flank of the belt, at the contact with the NMZ, many pegmatite bodies occur within the greenstones. Emeralds are found at the contact of deformed pegmatite and greenstone.

The greenstones mainly consist of actinolite and cummingtonite schists, containing various amounts of talc, chlorite, and albite. The association of acti-

nolite, chlorite and albite indicates greenschist-facies conditions. Although intense ductile deformation and regional metamorphism have obliterated most primary fabrics, the greenstones frequently contain relic olivine and pyroxene, indicating an ultramafic igneous nature of the initial protolith (Fig. 2).

The Fe-poor actinolite- and cummingtonite-dominated greenstones of the MGB in the vicinity of the emerald deposits may be interpreted as being a series of metamorphosed komatiites and, possibly, komatiitic basalts (compare, e.g., [12]). It is probable that the olivine-rich rocks in the MGB indicate an original olivine accumulation in komatiitic lava. This conclusion is supported, at one location, by the presence of titanian clinohumite, which normally occurs in serpentinised ultrabasic rocks (e.g., [9]), and by a preserved succession of cumulate textures, overlying giant spinifex fans and random pyroxene and olivine spinifex, described by Fedo and Eriksson [7], in the northeastern continuation of the Mweza Greenstone Belt (the Buhwa Greenstone Belt). These subunits are similar to komatiite flows described by, e.g., Wilson and Versfeld [27]. Significantly, emeralds are only found very near the contact between the greenstones and intrusive pegmatites at the southern flank of the greenstone belt. Other minerals that are typically present at this contact are albite, phlogopite, cummingtonite, actinolite, holmquistite, fluorapatite, chromian ilmenorutile, and less frequently, phenakite and chromite [29]. Fluids driven by intense shearing at the contact-zone between pegmatites and greenstones are responsible for chemical exchanges involving both country-rocks: intensive albitisation of pegmatite provoked release of potassium, which caused the formation of phlogopite in the inclosing greenstone. Cr and Mg originating from greenstone were incorporated into emerald. The reactivity of the fluid was enhanced by the presence of notable quantities of Li, F and P, further incorporated in the accessory minerals accompanying the emerald paragenesis, and in emerald itself (high Li and Cs content, Li: 800 ± 310 ppm, Cs: 710 ± 320 ppm [2]). The presence of typical pegmatite elements, notably Li, Be, F, P, Cs, Nb and Ta, indicates that, most likely, the pegmatite was a major fluid source.

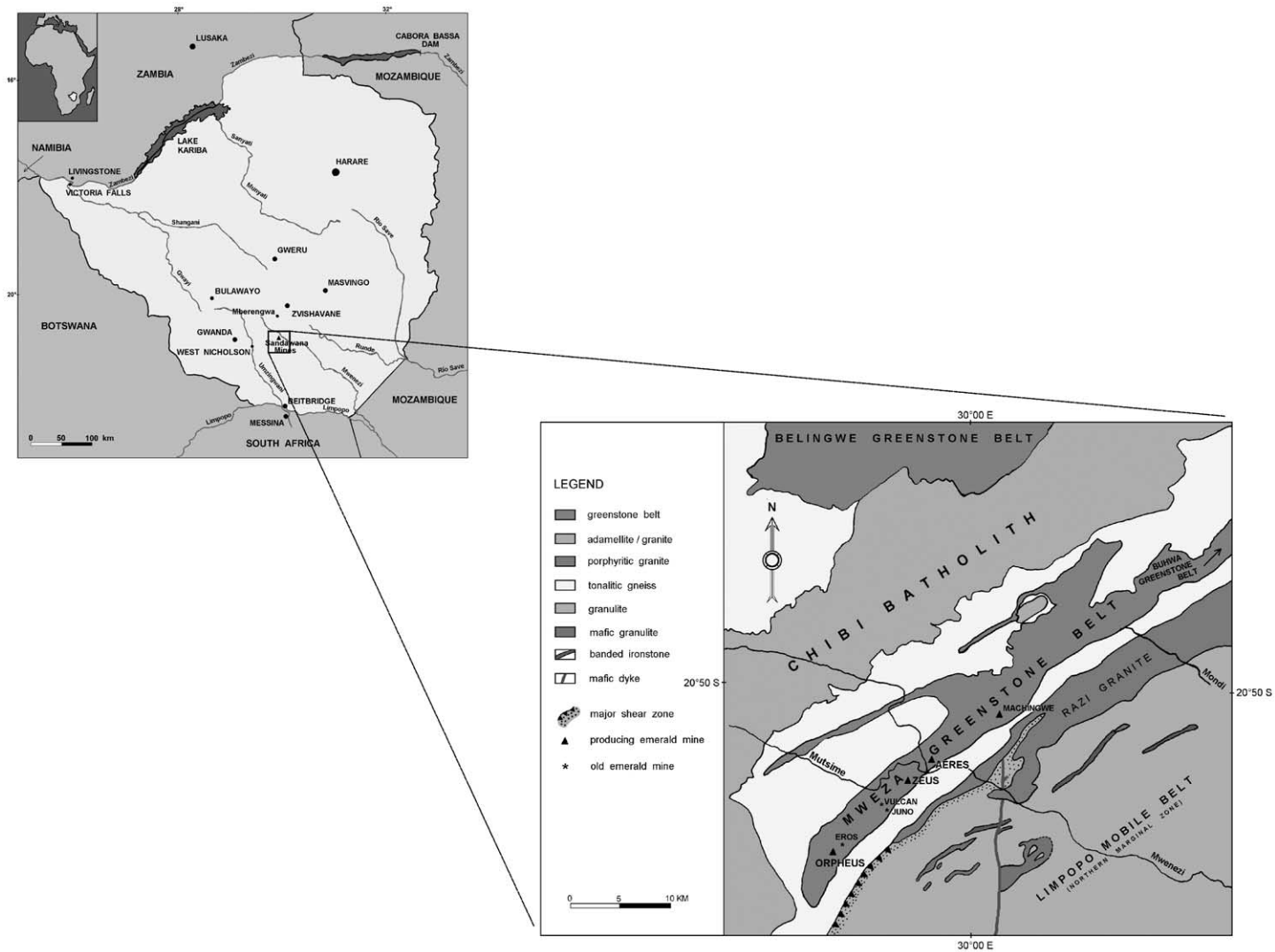


Fig. 1. The Sandawana emerald mines are located in southern Zimbabwe. The simplified geological map shows the location of the currently producing emerald mines, near the major shear zone that marks the border between the Zimbabwe craton and the Limpopo Mobile Belt. This map is mainly based on data of Robertson [22], Mkweli et al. [19] and satellite images.

Fig. 1. Carte simplifiée des principales mines d'émeraude de Sandawana, Sud du Zimbabwe. Les mines en activité sont situées le long l'accident important entre le craton du Zimbabwe et la ceinture mobile du Limpopo (d'après Robertson [22], Mkweli et al. [19] et images satellite).

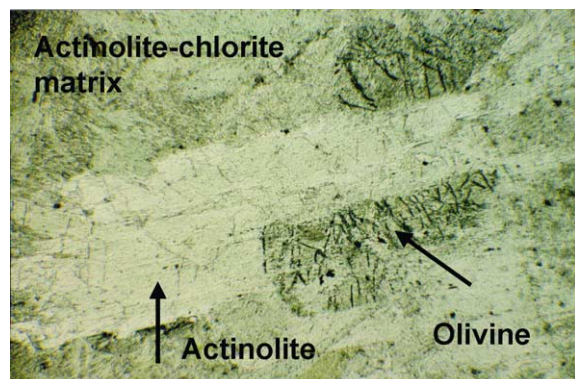


Fig. 2. The frequent presence of relic olivine and pyroxene indicates an ultrabasic igneous nature of the initial protolith. Intense ductile deformation and regional metamorphism obliterated the original fabrics. Here, an olivine, partly altered to serpentine and magnetite, was overgrown by actinolite (width of view: 2.4 mm).

Fig. 2. Composition ultrabasique du protolithe, indiquée par la présence fréquente d'olivine et pyroxène reliques. Actinote croissant sur olivine, partiellement altérée en serpentine et magnétite (largeur de la photo : 2,4 mm).

3. Oxygen isotope studies

Four emeralds from Sandawana, Zimbabwe, were used for analysis. Three emeralds were chosen from the largest underground operation at Sandawana, the Zeus Mine. Samples were taken on the 200, 225, and 300 feet levels, corresponding to a depth below surface of approximately 61.0, 68.6 and 91.4 m, respectively. The ore zones are all very narrow, normally up to only 15 cm width, but sometimes to a maximum of 30 cm width, with gem-quality emerald production from the actinolite-cummingtonite-phlogopite schist, at the contact with pegmatite. At the Orpheus mine, located 11 km southwest of the Zeus mine (Fig. 1), the emeralds are mined from an open pit. The chosen sample from this occurrence was mined from a weathered zone, close to the surface, from essentially the same amphibole-phlogopite schist found in close contact with pegmatite in the Zeus mine.

For comparison one emerald from the Belmont mine, Minas Gerais, Brazil, and one emerald from Habachtal, Austria, were also analysed.

3.1. Analytical technique

Oxygen isotope analysis was carried out at the Geological Survey of Canada, Ottawa, on powdered

Table 1
Results of $\delta^{18}\text{O}$ measurements in Sandawana emeralds

Tableau 1 Resultats des analyses $\delta^{18}\text{O}$ des émeraude de Sandawana		
This study	Sample No.	$\delta^{18}\text{O}$ (‰)
Locality at Sandawana		
Zeus mine, 200' level, 25/28 stope	RGM 421629	+6.6
Zeus mine, 225' level, 25/27 stope	RGM 466002	+7.2
Zeus mine, 300' level, 23/7 stope	RGM 421620	+6.9
Orpheus mine	RGM 421622	+7.4
Previous work [11]		
Locality at Sandawana		
Unknown	SAND-1	+8.0
Unknown	SAND-2	+6.9

aliquots of pure, hand-picked emerald using conventional methods of fluorination employing BrF_5 in externally-heated nickel vessels [5]. Mass spectrometry was performed on CO_2 using standard IRMS procedures in a FinniganMAT 252 spectrometer.

Data are reported in the usual δ -notation (permil, ‰), on the normalized V-SMOW-SLAP scale. Values of $\delta^{18}\text{O}$ reported for emerald have an over-all reproducibility of ca. 0.2‰. Our value of $\delta^{18}\text{O}$ for NBS-28 (African Glass Sand; IAEA-RM 8546) is 9.6‰.

3.2. Results

$\delta^{18}\text{O}$ values for the four Sandawana emeralds are given in Table 1 and compared with previous measurements done by Giuliani et al. [11] (Fig. 3). Our results are very homogeneous ($\pm 0.8\%$ variation range, $\delta^{18}\text{O}\text{‰} = +7.0 \pm 0.4$), slightly lower, but within the same error range than the $\delta^{18}\text{O}$ values given in [11]: $\delta^{18}\text{O}\text{‰} = +7.5 \pm 0.5$. Considering these two studies, the mean value for the Sandawana emerald is $\delta^{18}\text{O}\text{‰} = +7.3 \pm 0.7$.

Comparable $\delta^{18}\text{O}$ values are found in various other deposits in the world (Fig. 3). Similar values were measured for emeralds from Habachtal, Austria ($\delta^{18}\text{O}\text{‰} = +7.1 \pm 0.1$ [11]; $\delta^{18}\text{O}\text{‰} = +7.0$, this study), Poona, Australia ($\delta^{18}\text{O}\text{‰} = +7.25 \pm 0.25$ [11]) and various other non-economic deposits in Brazil (Juca: $\delta^{18}\text{O}\text{‰} = +6.8$; Pombos: $\delta^{18}\text{O}\text{‰} = +7.5$; Santana dos Ferros, $\delta^{18}\text{O}\text{‰} = +7.9$; all three in [11]). Also, a single oxygen isotope value from the Maria deposit, Mozambique ($\delta^{18}\text{O}\text{‰} = +8.2 \pm 0.2$

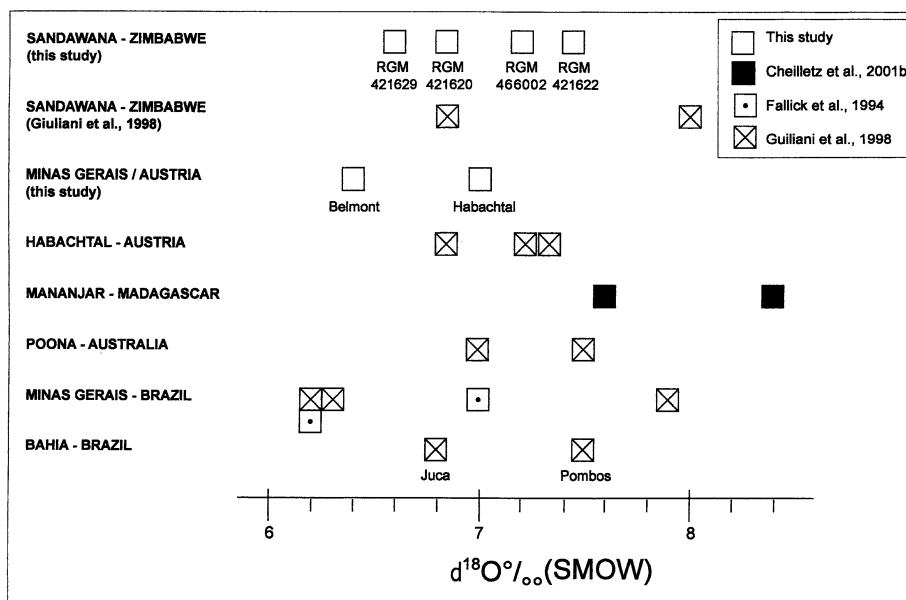


Fig. 3. $\delta^{18}\text{O}$ values of emerald for different deposits in the world compared to the $\delta^{18}\text{O}$ values obtained for the Sandawana-Zimbabwe deposit. $\delta^{18}\text{O}$ values obtained for the Belmont mine (Minas Gerais, Brazil) and Habachtal (Austria), correspond to our new measurements for these deposits.

Fig. 3. Valeurs de $\delta^{18}\text{O}$ d'émeraudes de divers gisements mondiaux, d'après la littérature et de nouvelles analyses – ce travail pour Sandawana, Zimbabwe, la mine de Belmont (Minas Geraes, Brésil) et Habachtal (Autriche).

[11]) is indistinguishable from the Sandawana SAND-1 value ($\delta^{18}\text{O}\text{‰} = +8.0 \pm 0.2$; Table 1 [11]).

The economically important deposits of the Quadrilatero Ferrifero, Minas Gerais, Brazil, comprise a wider range of values (Capoeirana: $\delta^{18}\text{O}\text{‰} = +6.2 \pm 0.3$ [6,11]; Belmont: $\delta^{18}\text{O}\text{‰} = +6.4$, this study; Itabira: $\delta^{18}\text{O}\text{‰} = +7.0 \pm 0.3$ [6]) with some overlapping (within error range) with the Sandawana emerald $\delta^{18}\text{O}$ values ($\delta^{18}\text{O}\text{‰} = +7.3 \pm 0.7$).

Emeralds from the Mananjara deposit in Madagascar have $\delta^{18}\text{O}$ values ranging from +7.6 to 8.7‰ [4], which partly overlap the $\delta^{18}\text{O}$ values determined for the Sandawana emeralds ($\delta^{18}\text{O}\text{‰} = +7.3 \pm 0.7$, this study).

Relative to the wide range of oxygen isotopic composition of emerald in the world (between +6.2 and +24.7‰ [11]), the $\delta^{18}\text{O}$ values of emeralds from the Sandawana mines are among the lowest measured. Only emeralds from Capoeirana and Belmont (Minas Gerais, Brazil) have lower values of $\delta^{18}\text{O}\text{‰} = +6.2$ and +6.4, respectively.

4. Discussion

4.1. Oxygen isotope signature of Sandawana emeralds

The very narrow ore zone (most often only 15 cm wide) in both the Orpheus Mine and the Zeus Mine at the contact of greenstones with pegmatite is representative for the whole emerald-bearing belt. All gem-quality emeralds from the Sandawana area come from exactly the same rock-type, i.e. an actinolite-cummingtonite-phlogopite schist, representing a metasomatized greenstone, corresponding to a series of metamorphosed komatiites.

As pointed out by Fallick et al. [6] and Cheilletz et al. [3], host-rock buffering plays an important role in establishing the oxygen isotope composition of emerald. The range of $\delta^{18}\text{O}$ values in metamorphosed komatiites, including modern komatiites from Gorgona, is relatively narrow, between +5 and +8‰ [18]. Komatiites from the nearby Belingwe greenstone belt, for example, have $\delta^{18}\text{O}$ values between +5.5 and +7.0,

somewhat higher than $\delta^{18}\text{O}$ values of komatiites from Barberton ($\delta^{18}\text{O} = +5.5 \pm 0.25\text{‰}$).

The other rocks involved in the genesis of emeralds, namely pegmatitic lenses, have a more variable and significantly higher $\delta^{18}\text{O}$ signature [25]. However, the narrow range of oxygen isotope composition in Sandawana emeralds, which overlaps with the komatiites, shows no influence of the metasomatised pegmatite, in line with the very low volume of these rocks compared to the greenstones. Entire isotopic homogenisation took place through fluid–rock buffering during regional metamorphism, but the signature was imprinted by the mantle-derived original protolith (komatiite). Similar conclusions can be drawn from the Habachtal deposit in Austria, for which, like for Sandawana, a metamorphic model has been proposed, involving interaction with serpentinites [14,21]. However, in this case, the serpentinites are much younger than those in Sandawana in as much as peak metamorphism occurred during the Middle Alpine *Tauernkristallisation*, between 65 and 35 Ma [13], and were derived from deep-seated (plutonic) ultrabasics (harzburgites or lherzolites). Yet, the oxygen isotope signature ($\delta^{18}\text{O}\text{‰} = +7.1 \pm 0.1$) of Habachtal emeralds matches exactly the values of those from Sandawana (Fig. 3), suggesting that the $\delta^{18}\text{O}$ composition of emerald is a reliable indicator of the geological environment, independent of time or age.

4.2. Oxygen isotope and chemical analysis: limits to distinction of the origin of cut emeralds

The traditional method of oxygen isotope analysis, used in this study, is a destructive technique, not applicable to expensive, gem-quality cut emeralds. Spot analysis by ion microprobe, however, produces only invisible craters of 10 to 20 micron in diameter and a few angströms deep. Ion microprobe analysis could, therefore, be done on emeralds of any commercial or historical value [10]. The ion microprobe is less accurate though, than the traditional method: the 1σ analytical precision, using the ion microprobe is $\pm 0.6\text{‰}$, instead of $\pm 0.2\text{‰}$ (traditional method). Nevertheless, it would be wrong to assert that oxygen isotope analysis, alone, is a ‘miracle tool’, able to identify the origin of any emerald without ambiguity, and without consideration of other criteria.

Emeralds from the commercially mined occurrences, at Sandawana (Zimbabwe), Habachtal (Austria), Minas Gerais (Brazil) and, partly Mananjar (Madagascar), show overlapping $\delta^{18}\text{O}$ values. Thus, in these cases, oxygen isotopic analysis cannot be used to establish their origin.

Emeralds from the above occurrences can be identified relatively easily, using other, more traditional gem-testing techniques. Refractive indices and densities are not very useful either in these particular cases, because they all fall in the same range (refractive indices 1.574–1.597, birefringence 0.005–0.009, densities 2.68–2.77 [16,30]). Except for emeralds from Habachtal with the lower values, they are useful, however, to distinguish emeralds from these localities, from those from the most important commercial sources in Colombia, whose emeralds have refractive indices of 1.569–1.580, birefringence of 0.005–0.007, and densities of 2.69–2.70 [15,26]). Colombian emeralds can be distinguished from the other sources noted by their omnipresent, highly diagnostic, irregularly shaped, three-phase brine inclusions. In this respect, of commercially available emeralds, only emeralds from central Nigeria, and Afghan emeralds from the Panshijr Valley are known to also contain three-phase or multiphase brines, which in some cases may appear similar to the inclusions in Colombian emeralds [1,17].

In contrast to those in Sandawana emeralds, fluid inclusions are abundant in emeralds from Minas Gerais [16,28], which feature narrow growth tubes, orientated parallel to the *c*-axis, that produce the well-known ‘rain effect’, often seen in aquamarine. Other characteristic inclusions are rectangular to almost square-shaped cavities, filled with CO_2 -rich fluids. Thus, whereas fluid inclusions in emeralds from some localities have unique characteristics, such properties must be used in conjunction with other features to confirm an emerald’s geographic locality.

Solid inclusions in emeralds may also vary from locality to locality. Although Habachtal emeralds typically contain amphibole rods, apatite crystals and phlogopite platelets, like the Sandawana material, these emeralds normally show an inhomogeneous ‘patchy’ color distribution [20] that has not been observed in Sandawana emeralds. Also, unlike in Habachtal emeralds, phlogopite is uncommon as an inclusion in Sandawana emeralds.

With respect to chemical composition, emeralds from Sandawana contain high MgO (2.5–2.8 wt%) and Na₂O content (2.1–2.4 wt% [30]), compared to the emeralds from Itabira, Minas Gerais (MgO: 0.5–1.9; Na₂O: 0.3–1.3 [16]). Additionally, various analyses (electron microprobe, PIXE) of cut and rough Habachtal emeralds show distinctly lower chromium content (Cr₂O₃ 0.01–0.44 wt% [23]; Cr₂O₃ 1390 ± 720 ppm [2]) than Sandawana emeralds (Cr₂O₃ 0.61–1.33 wt% [30]; Cr₂O₃ 5211 ± 2190 ppm; Calligaro et al. [2]). It should be noted, however, that at the rim of Habachtal emerald crystals Cr₂O₃ up to 0.91 wt% was measured [14], and according to Grundmann (pers. comm.), in some cases their chromium content can even go up to 1.14 wt%.

In other cases, there are situations, however, in which oxygen isotopic compositions can, indeed, be effectively used as an additional diagnostic tool. Solid inclusions found in Sandawana emeralds can very closely resemble inclusions found in emeralds from Rajasthan (India), which include ‘tremolite’ fibres very similar to the actinolite/cummingtonite fibres, typical of Sandawana emeralds [8]. Although other inclusions are very different (rectangular multiphase fluid inclusions in emeralds from Rajasthan), and despite a virtual absence of fluid inclusions in Sandawana emeralds, refractive indices and densities are also very similar (e.g., compare Gübelin [15] and Zwaan et al. [30]), and yet a somewhat ambiguous picture might arise, when examining a cut stone with an unknown origin. Oxygen isotopic compositions of these two localities are very different and can be diagnostic: $\delta^{18}\text{O}\text{‰} = +7.3 \pm 0.7$ (Sandawana), vs. $+10.8$ (Rajasthan [10]).

Further, long-prismatic amphibole rods and fibrous aggregates of talc frequently found in emeralds from Mananjar (Madagascar) may also look very similar to the amphibole fibres found in Sandawana emeralds [24]. However, in many Mananjar emeralds, phlogopite is the most common inclusion, and fluid inclusions also occur. $\delta^{18}\text{O}$ values of Mananjar emeralds have a larger range ($+7.6$ to 9.5‰ [4]), but partly overlapping with that of the Sandawana emeralds (Fig. 3), making oxygen isotope discrimination not totally secure as the distinguishing diagnostic tool for these two deposits. Thus, distinguishing source localities among emeralds is generally best approached by comparison of many features.

5. Conclusion

The relatively low $\delta^{18}\text{O}$ values of emeralds from the Sandawana mines, Zimbabwe, reflect the buffering of the isotopic system by metasomatised ultramafic host rocks during the metamorphic-driven formation of these emeralds. The $\delta^{18}\text{O}$ value of the fluid was controlled by the ultramafic nature of the greenstones, and the intensity of the fluid–rock interactions at the sheared and porous schist at the contact with the pegmatite. At any time during Earth’s history, emeralds formed in a comparable geological (lithological) environment can readily have comparable oxygen isotope compositions. Therefore, traditional gem testing techniques can often better fingerprint the locality origin of commercially available emeralds. In cases of overlapping physical and chemical properties, and ambiguous inclusion characteristics, as for the deposits of Sandawana (Zimbabwe) and Rajasthan (India), the use of oxygen isotopes may be helpful.

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