CRITICAL COMMENT


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INTRODUCTION

Suzuki et al. (2001) interpret inaccurate and irreproducible Re-Os molybdenite dates from the Galway granite, Ireland, to indicate that Re-Os systematics in this mineral have been disturbed by younger fluid interaction. Although this interpretation supports conclusions from two other studies (McCandless et al., 1993; Suzuki et al., 2000), it is at discord with many other studies, which demonstrate the highly robust nature of the Re-Os molybdenite chronometer (e.g., Stein et al., 1997, 1998a, 1998b; Frei et al., 1998; Watanabe et al., 1999; Watanabe and Stein, 2000; Raith and Stein, 2000; Selby and Creaser, 2001a, b; Selby et al., 2002; Stein and Bingen, 2002; Bingen and Stein, 2003). The disparity between the conclusion drawn by Suzuki et al. (2001) of disturbance to the Re-Os molybdenite system, and the conclusions of the many studies noted above, raises some concern for the perceived reliability of the molybdenite Re-Os chronometer in the geological community. In response, we present here accurate and reproducible Re-Os molybdenite dates from Galway Murvey and Galway Mace of the Galway granite, Ireland, previously investigated by Suzuki et al. (2001), and suggest that inaccurate and irreproducible Re-Os molybdenite dates of Suzuki et al. (2001), relate to inadequate sample preparation methods.

SAMPLES AND ANALYTICAL METHODOLOGY

For Galway Mace, the same sample used by Suzuki et al. (2001) was used here, but for Galway Murvey, a new sample was collected from the same location as the original (figure 1, location 1 and 2 of Suzuki et al., 2001). Molybdenite descriptions were not reported by Suzuki et al. (2001), and thus are given here. For Galway Mace, abundant molybdenite of 2 to 4 mm size occurs disseminated and as rosettes of ~1 cm diameter on the vein margin adjacent to alteration selvage. For Galway Murvey, minor disseminated molybdenite of 1 to 4 mm is present within the granite. A full mineral separate was obtained for each sample using conventional isolation techniques (cf., Selby et al., 2003), yielding ~2 g of molybdenite for the Galway Mace sample, and a total of 900 mg molybdenite from ~9 kg of rock for Galway Murvey. The 187Re and 187Os concentrations in molybdenite were determined from an aliquot (Table 1) of the mineral separate by isotope dilution mass spectrometry at the University of Alberta Radiogenic Isotope Facility using Carius tube, solvent extraction and chromatographic techniques (Selby and Creaser, 2001a). Rhenium and Os isotope ratios were measured using negative thermal ionization mass spectrometry (Creaser et al., 1991; Völkening et al., 1991) on a Micromass Sector 54 mass spectrometer using Faraday collectors. The Re-Os data for the Galway Mace and Galway Murvey molybdenite samples are presented in Table 1.

RESULTS

The Re and 187Os contents and Re-Os dates of
molybdenite from this study contrast with those reported by Suzuki et al. (2001) (Table 1). Firstly, our Re and 187 Os contents are highly reproducible for replicate analyses of the same sample. Secondly and importantly, the derived Re-Os dates are highly reproducible, and are indistinguishable within uncertainty of the U-Pb zircon age of the host Galway granite (412 ± 15 Ma, Pidgeon, 1969 (recalculated using the U decay constants of Jaffey et al., 1971)).

**DISCUSSION**

Suzuki et al. (2001) propose that discrepancies observed in their Re-Os dates are not the result of analytical protocols (microwave digestion, Re and Os measurements by ICP-MS), because replicate analyses of the HLP-5 “control” sample used by the AIRIE group, Colorado State University, yielded an age of 220.0 ± 2.1 Ma (n = 4). These dates are in agreement with those reported by Stein et al. (1997) (221.5 ± 0.3 Ma) and Markey et al. (1998) (221.3 ± 0.2 Ma), which were obtained through the different techniques of alkaline fusion and NTIMS techniques. The HLP-5 Re-Os age reported by Suzuki et al. (2001) is also in agreement with an average Re-Os age of HLP-5 of 220.5 ± 0.5 Ma reported by Selby et al. (2003), obtained by Carius tube methods and NTIMS isotopic analysis. It is important to note that the HLP-5 “control” sample is a 2 kg powder concentrate (~44 µm) obtained from separating ~0.13 to 0.2 mm molybdenite (Du Andao, pers. comm., 2001) from the Huanghaiopu deposit (Stein et al., 1997), and thus represents a large, pulverised, homogenous sample. For HLP-5 it has been previously shown that sub-milligram fractions do yield identical dates to those obtained from ~25 mg aliquots (Selby and Creaser, 2001a, b).

The analysed molybdenite samples of Suzuki et al. (2001) were described as being hand picked from quartz veins and granite. This method was apparently chosen instead of obtaining a mineral separate (Stein et al., 1998a, 2001; Selby et al., 2003), on the assumption that analysing aliquots from an pulverised, homogenised mineral separate might not yield the “true” formation age due to the homogenisation of potentially altered and unaltered molybdenite (Suzuki et al., 2000). This putative “variable alteration” mechanism in molybdenite is not supported by the determination of identical Re-Os molybdenite dates from a pulverised versus unpulverised very fine-grained sample (Selby and Creaser, 2001a).

Re-Os analysis of low milligram amounts of molybdenite, either hand picked or as single pieces of larger molybdenite grains has been shown to yield Re-Os dates that deviate significantly, either older and younger, from the “true” age obtained from an aliquot of a mineral separate (Stein et al., 1998a, 2001; Creaser and Selby, 2002; Selby et al., 2003). This effect relates to the physically decoupled nature of Re and 187 Os within molybdenite (Kosler et al., 2000; Stein et al., 2001, 2003; Creaser and Selby, 2002; Selby et al., 2003), demonstrated from laser ablation ICP-MS analyses that for one sample yield highly variable Re-Os dates of 0.5 to 4.0 Ga, in stark contrast to the highly reproducible Re-Os dates obtained from a fraction (~50 mg) of a mineral separate by Carius.

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Table 1. Re-Os isotopic data for molybdenite from the Galway Granite, Ireland

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Sample wt. (mg)</th>
<th>Total Re (ppm)</th>
<th>187Re (ppm)</th>
<th>187Os (ppb)</th>
<th>Re-Os age (Ma)</th>
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<tbody>
<tr>
<td><strong>This study</strong></td>
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<tr>
<td>Galway Mace</td>
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<tr>
<td>MH-19-1-1</td>
<td>10.6</td>
<td>75.74 ± 0.36</td>
<td>47.60 ± 0.23</td>
<td>324.1 ± 1.4</td>
<td>407.3 ± 1.5</td>
</tr>
<tr>
<td>MH-19-2</td>
<td>19.6</td>
<td>75.92 ± 0.27</td>
<td>47.72 ± 0.17</td>
<td>325.0 ± 0.9</td>
<td>407.3 ± 1.5</td>
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<tr>
<td>Galway Murvye</td>
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<tr>
<td>MH-1-1</td>
<td>102.8</td>
<td>5.14 ± 0.01</td>
<td>23.2 ± 0.01</td>
<td>22.16 ± 0.04</td>
<td>410.5 ± 1.5</td>
</tr>
<tr>
<td>MH-1-2</td>
<td>102.7</td>
<td>5.09 ± 0.01</td>
<td>23.2 ± 0.01</td>
<td>21.97 ± 0.04</td>
<td>410.8 ± 1.4</td>
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<tr>
<td><strong>Suzuki et al. (2001) data</strong></td>
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<td>Galway Mace</td>
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<tr>
<td>MH-19</td>
<td>76.14 ± 0.36</td>
<td>340.2 ± 1.9</td>
<td>425.2 ± 3.1</td>
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<tr>
<td>Galway Murvye</td>
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<tr>
<td>Analysis 1</td>
<td>9.492 ± 0.04</td>
<td>38.21 ± 0.79</td>
<td>383.2 ± 8.1</td>
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<tr>
<td>Analysis 2</td>
<td>10.95 ± 0.08</td>
<td>49.05 ± 0.51</td>
<td>426.1 ± 5.5</td>
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</table>

Note: Total procedural blanks were 2.5 pg for Re and 0.5 pg for Os, which are insignificant in comparison to the Re and Os amounts analyzed. All uncertainties are reported at the 2σ absolute level. Re-Os dates were determined using the 187Re decay constant of Smoliar et al. (1996) (1.666 × 10^-11 a^-1).

1 Mineral separate obtained from same sample used by Suzuki et al. (2001).
2 Mineral separate obtained from a sample collected from the same locality that Suzuki et al. (2001) investigated.
tube dissolution and ID-NTIMS (2809 ± 1.7 Ma) (Stein et al., 2001). The internal decoupling of Re and 187Os may yield “erroneous” Re-Os dates if too small an aliquot of the mineral is used, especially in coarse-grained and old samples (Stein et al., 2001; Creaser and Selby, 2002; Selby et al., 2003).

To obtain accurate and reproducible Re-Os dates from molybdenite, we have found that use of an aliquot from a mineral separate is necessary, as demonstrated here, and as Suzuki et al. (2001) have also observed for their analyses of the HLP-5 “control” sample. This approach has been used for many locations where molybdenite has a genetic relationship with a magmatic or metamorphic event, and the Re-Os date obtained for molybdenite from an aliquot of a mineral separate is in excellent agreement with independently determined U-Pb dates for either magmatism or metamorphism (Ootes et al., 2002; Selby et al., 2002, 2003, this study; Stein and Bingen, 2002; Bingen and Stein, 2003). Many other molybdenite studies from geologically complex environments demonstrate the robust nature of the Re-Os chronometer in this mineral (Stein et al., 1997, 1998b, 2001; Frei et al., 1998; Watanabe et al., 1999; Watanabe and Stein, 2000; Raith and Stein, 2000; Selby and Creaser, 2001a; Selby et al., 2001).

The Re-Os molybdenite dates presented here from the Galway granite, are in agreement with the existing age constraints for the associated granite, and do not support a conclusion of disturbance to Re-Os systematics by younger hydrothermal fluids. Similarly, Stein et al. (2001) demonstrated for the Lobash deposit, Re-Os molybdenite dates display closed-system behaviour and yield precise, reproducible dates, whereas discordant Re-Os molybdenite dates from Lobash determined by Suzuki et al. (2000) were interpreted to represent disturbance to the Re-Os systematics.

We suggest that the inaccurate and irreproducible Re-Os data of Suzuki et al. (2001) are a direct result of the protocol used in the preparation of the molybdenite analysed, and through their methodology they have not minimised the decoupled nature of Re and 187Os in molybdenite sufficiently to obtain accurate and reproducible Re-Os dates.

**REFERENCES**


