

$\delta^{18}\text{O}$ of igneous chromites: an indicator of syn- and post-magmatic hydrothermal interaction

D. Lowry
N. V. Grassineau
E. G. Nisbet
D. P. Mattey

Department of Geology, Royal Holloway University of London,
Egham, Surrey TW20 0EX, UK

Chromites are commonly found in the basal units of komatiites, ophiolites and layered intrusions. They carry much information about the tectonic setting and magmatic origins of their host rocks and have an close relationship with sulphides and platinoid-group minerals. The oxygen isotopes of chromites and chrome spinels show a large fractionation from the host magma and the silicate minerals with which they co-exist. This means that chromite formation is extremely sensitive as an isotope thermometer. Samples of chromite have been analysed to assess: a) the influence of chromite crystallisation on magmatic and mineralisation processes, and b) the degree of interaction with hydrothermal fluids.

Analytical techniques

Chromites and co-existing silicates were separated from 125 μm and 250 μm size fractions by hand-picking. The minerals were analysed using two different wavelength IR laser fluorination (BrF_5) systems: olivine and clinopyroxene using a Nd-YAG

laser and feldspar using a CO_2 laser. Chromite was analysed on both systems to test the reaction systematics. In the middle of the reaction a dense covering of fluoride residue forms. This acts as a barrier to the Nd-YAG laser often resulting in incomplete oxygen yields, but is still penetrable by the CO_2 laser. Oxygen yields were consistently higher using the CO_2 system. Microprobe analyses of representative grains from the separates were used to calculate yields of oxygen. Those analyses which give 80–90% yields of oxygen have isotope ratios 0.2–0.3‰ lower than the same samples yielding 92–99% oxygen.

Chromites from platinum-enriched and platinum-deficient ophiolites

Representative chromite samples from the platinum-enriched Shetland ophiolite and the platinum-deficient Sakhakot-Qila ophiolite (Fig. 1) show significant differences in $\delta^{18}\text{O}$ which can be related to the degree of hydrothermal interaction. The

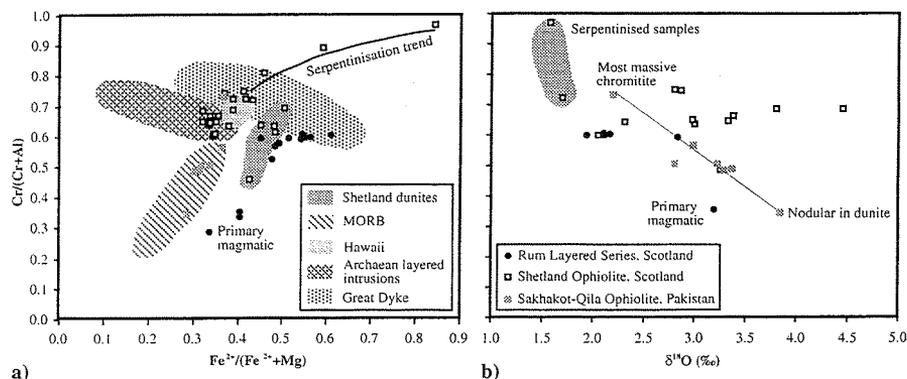


FIG. 1. Plots of $\text{Cr}/(\text{Cr}+\text{Al})$ versus a) $\text{Fe}^{2+}/(\text{Fe}^{2+}+\text{Mg})$, and b) $\delta^{18}\text{O}$, for ophiolitic and layered series chromites. Modern and ancient analogues are plotted for comparison (from Rollinson, 1995), together with the trends for serpentinisation.

Pakistan samples show a linear change from nodular chromite in dunite which has the highest spinel content (high Mg,Al) and the highest $\delta^{18}\text{O}$ value of 3.9‰, to massive chromitite with high Cr and Fe (Fig. 1a) and low $\delta^{18}\text{O}$ of 2.2‰ (Fig. 1b).

In contrast most Shetland samples have Cr/(Cr+Al) ratios between 0.6 and 0.7, the whole range being 0.45 to 0.95. The $\delta^{18}\text{O}$ ranges from 1.6–4.5‰ (Fig. 1b). The high Cr samples correlate with serpentinised rocks. These samples have low $\delta^{18}\text{O}$ values (<2.5‰); they are heterogeneous and proved difficult to extract high oxygen yields. The highest $\delta^{18}\text{O}$ values are for a large chromite lense and chromite nodules in dunite (3.8–4.5‰). Pyroxenites in dunites and wehrlites were analysed because of the absence of fresh silicates in lithologies surrounding the chromites. These yielded $\delta^{18}\text{O}$ values of $5.57 \pm 0.04\%$ (1 σ , n = 6) for pyroxene separates. Pyroxenes have oxygen isotopic compositions close to melt values. These Shetland values are typical of MORB and mantle pyroxenes (Mattey *et al.*, 1994), suggesting that the primary igneous chromites formed at 1000–1200°C in equilibrium with pyroxene.

Chromites from the Eastern Layered Series, Rum, Scotland

New samples from chromite seams and adjacent silicates, and from Units 1 and 2 of the Eastern Layered Series, show restricted ranges of isotopic composition for olivine and clinopyroxene (<0.3‰) throughout the sequence. These ranges are much smaller than conventional fluorination data suggests (1.6‰ for olivine and 2.2‰ for clinopyroxene, Hulbert *et al.*, 1992). Olivine and clinopyroxene values are lower than typical mantle/MORB values by 0.6‰ and 0.8‰, respectively, suggesting that Rum layered series is the product of low $\delta^{18}\text{O}$ magmas, like the neighbouring intrusives of the British Tertiary Igneous Province (e.g. Skye). Fractionation between olivine and clinopyroxene is relatively constant at 0.2‰, but both olivine and pyroxenes increase up the sequence from Units 1 to 10, possibly indicating less incorporation of low $\delta^{18}\text{O}$ altered crust during magma ascent.

The equations of Zheng (1993), which are applicable up to 1200°C, have been used to calculate possible equilibrium temperatures. The most realistic of these and the primary $\delta^{18}\text{O}$ of chromite are highlighted in bold. Mineral $\delta^{18}\text{O}$ values are reported relative to V-SMOW.

Chromite data shows two clear groupings (at 3.2‰ and 2.1‰); the higher representing primary

magmatic chromite containing a much larger spinel component (Fig. 1a). Plagioclase data covers a wide range of 6.6‰. Only one plagioclase sample has not undergone significant hydrothermal interaction. Fractionations between clinopyroxene (4.7‰), feldspar (5.2‰) and 3.2‰ chromites yield equilibrium temperature estimates of $1090 \pm 50^\circ\text{C}$, realistic for crystallisation. Plagioclase from unit tops show a variation in values between 5.2‰ and 0.9‰ which is related to the modal abundance. If $\delta^{18}\text{O}$ alteration by high temperature meteoric fluids was mostly subsolidus (Hulbert *et al.*, 1992), olivine and pyroxene would be expected to show wider isotopic variations. Mixing Eocene meteoric water (–12‰, Sheppard, 1986) with molten intercumulus plagioclase could explain the observed changes.

Plagioclase data is also notable for fractionations of 2.1–2.3‰ between feldspar abundant allivalite unit tops and minor feldspar which is interstitial to olivine in the base of the overlying peridotite units. Chromite values are lowered by 1.0–1.2‰, associated with a reaction alteration producing higher Fe and Cr toward the top of the layers (Dunham and Wilkinson, 1985). These shift of chromite and feldspar values may have occurred by reactions of residual melt at the top of the unit (plagioclase and volatiles?) with chromite and the rapidly settling olivine which formed the base of the new unit.

Conclusions

Primary igneous chromites react to give high yields of oxygen and consistent isotopic results. High yields are difficult to achieve with greater degree of recrystallisation and/or hydrothermal alteration of the chromites, and lower but inconsistent $\delta^{18}\text{O}$ values are recorded. In addition to zonation of the crystals this may in part be due to trapped fluids in the chromites. The lowering of $\delta^{18}\text{O}$ values by serpentinisation in the Shetland ophiolite and by high temperature hydrothermal interactions in the Rum layered series have been distinguished by analysis of chromites.

References

- Dunham, A.C. and Wilkinson, F.C.F. (1985) *Geol. Mag.*, **122**, 539–48.
- Hulbert, L.J. and 10 others (1992) *Mineral deposit modelling in relation to crustal reservoirs of the ore forming elements* Instn. Min. Metall., Keyworth, Extended abstract.
- Mattey, D.P., Lowry, D. and Macpherson, C.G. (1994) *E.P.S.L.*, **128**, 231–41.