Reply to ‘Discussion of oxygen isotopes in ophicalcites: an ever-lasting controversy?’ by R. Coltat, Ph. Boulvais, Y. Branquet, M. Poujol, P. Gautier and G. Manatschal

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Our publication ‘Oxygen isotopes in ophicalcites: an ever-lasting controversy?’ in this journal (Bernoulli and Weissert 2020) discussed the interpretation of oxygen isotopes in Alpine ophicalcites and deep-sea sediments. Based on the remarkable correlation of the isotope values with the degree of Alpine metamorphism (Bernoulli and Weissert 2020: Fig. 4), we argued that the oxygen isotope signatures measured in ophicalcites and pelagic limestones were equilibrated during Alpine metamorphism. They do not reflect the temperatures of carbonation of the serpentine host rocks or the formation of calcite in veins and cements or of marine biogenic calcite in pelagic sediments associated with the ophicalcites. In particular, we doubted the interpretation of Coltat et al. (2019a) that the oxygen isotope values in the ophicalcites of South-Penninic Platta Nappe at Falotta faithfully recorded the temperature of carbonation and of the emplacement of calcite veins in the serpentinite host rock, estimated by Coltat et al. (2019a) at ~100 °C. In contrast, the near-identical oxygen isotope values in the ophicalcites and in the overlying Upper Jurassic–Lower Cretaceous pelagic limestones clearly indicate that the Middle Jurassic ophicalcites and the overlying sediments underwent *together* one or more thermal events resetting their oxygen isotope signatures, which in contrast were related by Coltat et al. (2019a) exclusively to a ‘single, sudden event’ of hydrothermal activity during the Middle Jurassic.

We do not doubt the importance of hydrothermal fluids in the formation of ophicalcites (Früh-Green et al. 1990), nor that at Falotta carbonation of the serpentinite host rock occurred during the exhumation of mantle rocks along low-angle detachment faults (e.g. Desmurs et al. 2001), nor do we doubt deformation associated with ophicalcite

formation. We only relate the *present-day* oxygen values observed in the *ophicalcites and associated sediments* to Alpine metamorphism.¹

Coltat et al. (2019a, b, 2020) regard the localities Falotta and Marmorera–Cotschens as singularities where practically no Alpine fluid exchange or recrystallization occurred. However, we doubt that no Alpine recrystallization should have occurred at Falotta [see Fig. 5 in Bernoulli and Weissert (2020) for an example in the less metamorphic Totalp Nappe] and that no fluids circulated during Alpine deformation and metamorphism. That all calcite crystals in the ophicalcites at Falotta show identical $\delta^{18}\text{O}$ -values, irrespective of their habit (Coltat et al. 2019a:185, 2020), is, in our view, much better explained by Alpine metamorphic re-equilibration than by one single hydrothermal event.

Coltat et al. (2021) write that isotopic re-equilibration ‘*could be partly true*’ for post-rift sediments but they do not explain why this should be only partly true. We do not know of any pelagic limestones of Late Jurassic–Early Cretaceous age outside orogens showing oxygen isotope values of –6 to –14 ‰. These values can only be the result of metamorphic overprint. In addition, ophicalcites and pelagic limestones consistently show a parallel evolution along the entire transect from northern Graubünden to Val Malenco and *all* pelagic sediments show re-equilibrated values along it (Fig. 1). We are well aware that the oxygen isotope values are difficult to interpret and that different processes at different times have altered them; however, close correlation with metamorphic grade shows that re-equilibration occurred during Alpine metamorphism.

Coltat et al. (2020) distinguish between ‘cooler ophicalcites’ in the South-Penninic nappes and the ophicalcites of the Platta Nappe. However, at other localities like Arosa, the

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¹ We are well aware that this metamorphism occurred during the accretion of the upper plate units of Alpine subduction that were not subducted (see e.g. McCarthy et al. 2018). We said that subduction started in the Late Cretaceous, but not that the Platta Nappe was subducted, as insinuated by Coltat et al. (2021).

Fig. 1 Correlation between O-isotope composition of opicalcites and oceanic sediments, and metamorphic grade along a transect of the Penninic/Australpine boundary zone, Graubünden. From Bernoulli and Weissert (2020: Fig. 4), with the oxygen isotope values from Marmorera–Cotschens (Coltat et al. 2019b) added

opicalcites co-occur with basalts, similar to the opicalcites at Falotta (Platta Nappe). Likewise evidence for hydrothermal activity is seen in ‘cold opicalcites’ at Totalp and Gotschna where hydrogrossular, identified in opicalcites (Totalp, Früh-Green et al. 1990), is pointing at hydrothermal temperatures of up to 200 °C where no basalts occur.

In our paper (Bernoulli and Weissert 2020), we did not discuss the data from Marmorera–Cotschens. At these outcrops, Coltat et al. (2019b) measured in the calcite veins $\delta^{18}\text{O}_{\text{V-SMOW}}$ values of $\sim +12\text{‰}$, i.e. 4‰ lower than those measured at Falotta. We included these values now in our Fig. 1; they do not deviate much from the general trend in the N–S-transect and might reflect a somewhat higher grade of Alpine metamorphism: they are still in the range of greenschist metamorphism indicated for this locality by Ferrero Mählmann (1996, 2001). In fact, the outcrop at Marmorera is about 500 m deeper in the tectonic edifice than Falotta. In addition, the Late Jurassic–Early Cretaceous U–Pb age (144 ± 13 Ma) in calcite from Cotschens is much younger than the intrusion of the gabbros (161 ± 1 Ma, Schaltegger et al. 2002) to which hydrothermal activity is related according to Coltat et al. (2019a). Even though Epin et al. (2019) report the intrusion of a lone magmatic sill in the Lower Cretaceous Aptychus Limestone near Bivio, the significance of this Late Jurassic–Early Cretaceous numerical age is most uncertain. It is also much younger than the onset of deposition of the syn- to post-rift radiolarites that, however, in Graubünden is not precisely dated. An upper age bracket of radiolarite deposition is given by the age of the overlying Aptychus (Calpionella) Limestone (late Tithonian–Berriasian) dated

in the Davos region (Weissert 1975), a lower one by the general age of the onset of radiolarite deposition in the Liguria–Piemontese realm beginning in the Bathonian (168–166 Ma, Bill et al. 2001).

‘No low-temperature opicalcites have been found yet in the Alps, suggesting that their original low-temperature signatures have been obliterated by Alpine metamorphism’ (Bernoulli and Weissert 2020). Indeed no opicalcites with high $\delta^{18}\text{O}_{\text{V-SMOW}}$ values like of those recorded at the MAR or at the Newfoundland or Iberian margins are reported from the Alps, but could be expected if no or minor thermal alteration had taken place. We never excluded the existence of higher-temperature hydrothermal carbonates in present-day oceans as cited by Coltat et al. (2021); however, the existence of such higher-temperature carbonates in present-day oceans is no independent argument against Alpine re-equilibration of the oxygen isotopes. In fact also oxygen isotopes of ‘higher-temperature’ opicalcites, if present at Falotta or Cotschens, could still have been re-equilibrated during greenschist-grade Alpine metamorphism.

Coltat et al. (2019a, b, 2020) think that the near-identical oxygen isotope composition in opicalcites and the close correlation of these values and the Alpine metamorphic grade are fortuitous, admitting only that, ‘on some sites post-rift sediments display oxygen isotope signatures *roughly similar* to those of opicalcites and may indeed reflect a *local Alpine overprint*’ (Coltat et al. 2021). In particular, the overturned succession in Val Saviez (Weissert and Bernoulli 1985: Fig. 4) is cited to illustrate the particular circumstance under which a *local Alpine overprint* might occur. However, tectonically overturned successions are ubiquitous in the Platta Nappe and the Arosa Zone (e.g. Gotschna, Weissfluh/Davos) and show the same degree of metamorphism as their surroundings. This rather reflects the importance of Alpine tectonics related to ‘subduction initiation and accretion’ during the Late Cretaceous followed by Cenozoic collision (McCarthy et al. 2018). If the sediments at Rocabella display higher $\delta^{18}\text{O}_{\text{V-SMOW}}$ values it is because this locality is situated higher in the nappe pile in a Lower Austroalpine unit (Bernoulli and Weissert 2020: Fig. 2) of lower Alpine metamorphic grade (Ferrero Mählmann 1996, 2001).

We think that the principle of simplicity (Occam’s Razor) is still a valuable tool in science and that our correlation of oxygen isotope composition and metamorphic grade in *opicalcites and sediments* is not fortuitous but reflects a common cause. The ‘ever-lasting controversy’ may, therefore, not be solved.

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