**Appendix A. Supplementary data**

**Table S1. The values of chemical compositions of alkaline fluids produced near pyrometamorphic rocks.**

|  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Sample | Location | pH\*\*\* | Ca\* | Mg\* | Na\* | K\* | HCO3+CO3\*\* | SO4\* | Cl\* | reference |
| M1-7 | Eastern springs | 12.5 | 622 | < 0 | 34 | 16 | 2 | 284 | 68 | Khoury et al. (1992) |
| MQ-5 | Western springs | 12.4 | 1,050 | < 0 | 132 | 613 | 6 | 1,481 | 51 | Khoury et al. (1992) |
| MQ-6 | Western springs | 12.5 | 1,120 | < 2 | 193 | 771 | 1 | 1,671 | 45 | Khoury et al. (1992) |

\*The concentrations are expressed as integer values in ppm.

\*\*The CO3 ion concentration in mmol/L listed in Khoury et al. (1992) was calculated to ppm using the molecular weight of the CO3 ion, and listed in this paper as HCO3+CO3 concentration in ppm.

\*\*\*The pH is listed in one decimal place.

**Table S2. The values of chemical compositions of alkaline fluids produced near ophiolites.**

|  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Sample | Location | Type | pH \*\*\*\* | Ca\* | Mg\* | Na\* | K\* | HCO3+CO3\*\* | SO4\* | Cl\* | reference |
| V18 | Italy | Ca–OH | 11.4 | 23 | 0 | 17 | 2 | 2 | 4 | 12 | Bruni et al. (2002) |
| BR1 | Italy | Ca–OH | 11.9 | 47 | 0 | 24 | 3 | 1 | 0 | 21 | Bruni et al. (2002) |
| L43 | Italy | Ca–OH | 11.5 | 49 | 0 | 28 | 5 | 3 | 0 | 19 | Bruni et al. (2002) |
| S70 | Italy | Ca–OH | 11.4 | 36 | 0 | 5 | 2 | 1 | 18 | 23 | Bruni et al. (2002) |
| C11 | Italy | Ca–OH | 10.5 | 3 | 6 | 13 | 2 | 20 | 25 | 23 | Bruni et al. (2002) |
| A1 | Italy | Ca–OH | 11.6 | 44 | 0 | 13 | 1 | 2 | 13 | 27 | Bruni et al. (2002) |
| Gw1 | Norway | Mg–HCO3 | 9.6 | 2 | 7 | 10 | 0 | 30 | 3 | 15 | Okland et al. (2012) |
| Gw2 | Norway | Mg–HCO3 | 9.0 | 1 | 10 | 12 | 0 | 44 | 4 | 18 | Okland et al. (2012) |
| Gw3 | Norway | Mg–HCO3 | 8.8 | 1 | 10 | 13 | 0 | 48 | 4 | 19 | Okland et al. (2012) |
| OM15-1W | Oman | Mg–HCO3 | 8.2 | 15 | 61 | 20 | 1 | 283 | 36 | 35 | Giampouras et al. (2020) |
| OM15-2W | Oman | Mg–HCO3 | 8.8 | 13 | 59 | 23 | 1 | 242 | 46 | 43 | Giampouras et al. (2020) |
| OM15K-2W | Oman | Mg–HCO3 | 9.4 | 7 | 174 | 389 | 11 | 880 | 62 | 589 | Giampouras et al. (2020) |
| OM15K-7W | Oman | Mg–HCO3 | 8.2 | 17 | 69 | 26 | 1 | 349 | 34 | 50 | Giampouras et al. (2020) |
| OM15K-23W | Oman | Mg–HCO3 | 9.3 | 10 | 33 | 37 | 2 | 151 | 28 | 59 | Giampouras et al. (2020) |
| OM15-4W | Oman | Ca–OH | 11.7 | 72 | 0 | 120 | 5 | 60 | 0 | 182 | Giampouras et al. (2020) |
| OM15-9W | Oman | Ca–OH | 11.6 | 64 | 0 | 112 | 5 | 60 | 1 | 171 | Giampouras et al. (2020) |
| OM15K-1W | Oman | Ca–OH | 12.0 | 78 | 0 | 139 | 6 | 79 | 1 | 183 | Giampouras et al. (2020) |
| OM15K-3W | Oman | Ca–OH | 12.2 | 67 | 0 | 144 | 6 | 80 | 1 | 190 | Giampouras et al. (2020) |
| OM15K-4W | Oman | Ca–OH | 12.1 | 68 | 0 | 140 | 5 | 85 | 1 | 184 | Giampouras et al. (2020) |
| OM15K-9W | Oman | Ca–OH | 11.9 | 82 | 0 | 144 | 6 | 23 | 0 | 186 | Giampouras et al. (2020) |
| OM15K-11W | Oman | Ca–OH | 12.1 | 78 | 0 | 164 | 6 | 100 | 0 | 211 | Giampouras et al. (2020) |
| OM15K-14W | Oman | Ca–OH | 12.1 | 82 | 0 | 158 | 6 | 102 | 0 | 195 | Giampouras et al. (2020) |
| OM15-3W | Oman | Mix | 11.2 | 6 | 14 | 92 | 4 | 43 | 12 | 143 | Giampouras et al. (2020) |
| OM15-5W | Oman | Mix | 9.5 | 18 | 49 | 37 | 2 | 219 | 39 | 64 | Giampouras et al. (2020) |
| OM15-6W | Oman | Mix | 9.7 | 17 | 46 | 43 | 2 | 226 | 36 | 73 | Giampouras et al. (2020) |
| OM15-8W | Oman | Mix | 10.5 | 6 | 29 | 70 | 3 | 94 | 22 | 110 | Giampouras et al. (2020) |
| OM15-11W | Oman | Mix | 10.7 | 8 | 26 | 77 | 3 | 80 | 20 | 115 | Giampouras et al. (2020) |
| OM15-12W | Oman | Mix | 10.5 | 6 | 25 | 77 | 3 | 87 | 21 | 117 | Giampouras et al. (2020) |
| OM15K-5W | Oman | Mix | 11.7 | 24 | 9 | 119 | 5 | 70 | 6 | 166 | Giampouras et al. (2020) |
| OM15K-6W | Oman | Mix | 10.7 | 14 | 18 | 106 | 4 | 121 | 12 | 148 | Giampouras et al. (2020) |
| OM15K-8W | Oman | Mix | 9.8 | 12 | 34 | 85 | 3 | 191 | 20 | 119 | Giampouras et al. (2020) |
| OM15K-10W | Oman | Mix | 10.4 | 14 | 22 | 100 | 4 | 106 | 14 | 138 | Giampouras et al. (2020) |
| OM15K-13W | Oman | Mix | 11.2 | 7 | 25 | 99 | 4 | 115 | 17 | 134 | Giampouras et al. (2020) |
| OM15K-16W | Oman | Mix | 11.6 | 20 | 5 | 126 | 5 | 61 | 10 | 160 | Giampouras et al. (2020) |
| OM15K-18W | Oman | Mix | 11.5 | 18 | 4 | 127 | 5 | 61 | 9 | 163 | Giampouras et al. (2020) |
| OM15K-19W | Oman | Mix | 10.4 | 5 | 0 | 200 | 8 | 105 | 1 | 269 | Giampouras et al. (2020) |
| OM15K-20W | Oman | Mix | 11.5 | 18 | 3 | 131 | 5 | n.p.m\*\*\* | 8 | 166 | Giampouras et al. (2020) |
| OM15K-21W | Oman | Mix | 11.5 | 14 | 2 | 135 | 5 | n.p.m\*\*\* | 7 | 170 | Giampouras et al. (2020) |
| OM15K-22W | Oman | Mix | 11.1 | 6 | 2 | 139 | 5 | 60 | 8 | 173 | Giampouras et al. (2020) |

\*The concentrations are expressed as integer values in ppm.

\*\*The dissolved inorganic carbon as HCO3 in mg/kg which was listed in Bruni et al. (2002) is exhibited as HCO3+CO3 concentration in ppm in this paper. The dissolved inorganic carbon in µmmol/L or mmol/L listed in Okland et al. (2012) and Giampouras et al. (2020) was calculated to ppm using the molecular weight of the CO3 ion and listed in this paper as HCO3+CO3 concentration in ppm.

\*\*\*Not possible to measure.

\*\*\*\*The pH is listed in one decimal place.

**Table S3. The values of chemical compositions of alkaline fluids in alkaline saline lakes.**

|  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Sample\*\* | pH | Ca\* | Mg\* | Na\* | K\* | HCO3+CO3\*\*\* | SO4\* | Cl\* | F\* | B\* | PO4\* | SiO2\* | Al\* |
| 2A | 9.2 | ― | ― | 60,000 | 1,720 | 1,100 | 45,700 | 79,500 | 125 | 470 | 0 | 52 | < 1 |
| 2B | 9.8 | ― | ― | 80,000 | 2,160 | 8,556 | 13,100 | 91,600 | 235 | 440 | 384 | 54 | < 1 |
| 2C | 9.9 | ― | ― | 70,000 | 1,820 | 10,050 | 9,910 | 85,600 | 228 | 270 | 398 | 61 | 2.8 |
| 2D | 9.7 | ― | ― | 114,000 | 3,180 | 24,140 | 19,000 | 114,000 | 465 | 360 | 657 | 66 | < 1 |
| 2E | 9.85 | ― | ― | 94,000 | 2,800 | 17,550 | 10,000 | 104,000 | 330 | 310 | 588 | 52 | 14 |
| 2F | 9.5 | ― | ― | 108,000 | 3,040 | 19,450 | 11,400 | 124,000 | 420 | 440 | 636 | 63 | 12 |
| 2G | 9.25 | ― | ― | 38,000 | 2,520 | 4,330 | 4,390 | 52,700 | 110 | 214 | 66 | 72 | < 1 |
| 2H | 9.6 | ― | ― | 112,000 | 6,200 | 17,270 | 14,900 | 131,000 | 223 | 719 | 1,318 | 44 | < 1 |
| 2I | 9.7 | ― | ― | 94,000 | 3,460 | 17,520 | 10,200 | 116,000 | 235 | 505 | 800 | 68 | 0.83 |
| 2J | 9.7 | ― | ― | 96,000 | 3,700 | 17,520 | 22,900 | 107,000 | 245 | 427 | 508 | 65 | 1.25 |
| 2N | 10.1 | ― | ― | 66,000 | 3,176 | 19,510 | 16,500 | 52,200 | 225 | 466 | 348 | 95 | 0.5 |
| 2O | 9.7 | ― | ― | 112,000 | 6,250 | 15,100 | 24,600 | 115,000 | 250 | 893 | 1,049 | 67 | 0.38 |
| 2P | 10.0 | ― | ― | 106,000 | 3,300 | 20,422 | 30,600 | 93,000 | 405 | 816 | 627 | 42 | 1 |
| 2Q | 9.6 | ― | ― | 116,000 | 4,100 | 14,800 | 30,600 | 118,000 | 310 | 816 | 710 | 52 | < 1 |
| 2V | 9.6 | ― | ― | 102,500 | 2,690 | 10,406 | 15,900 | 122,000 | 350 | 583 | 1,017 | 75 | 0.63 |
| 2W | 9.6 | ― | ― | 104,000 | 2,490 | 13,800 | 12,300 | 120,000 | 330 | 544 | 786 | 55 | < 1 |
| 2X | 9.7 | ― | ― | 110,000 | 3,680 | 13,822 | 20,000 | 124,000 | 250 | 699 | 800 | 68 | < 1 |

\*The concentrations are expressed as integer values in ppm.

\*\*Data are chemical compositions of the interstitial brined associated with the tuff bed at Teels Marsh and sourced from Taylor & Surdam (1981).

\*\*\*The concentration of HCO3 in ppm plus the concentration of CO3 in ppm is exhibited.

**Table S4. Summary of previous laboratory and in-situ experiments regarding C–(A–)S–H or tobermorite formation during the alkaline alteration of bentonite or clay.**

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| **Alkaline source** | **Primary minerals** | **Time** | **Temp [ºC]** | **Alteration of primary smectite**(Except for ion-exchange) | **Secondary minerals** | **Reference** |
| pH 12.6 Ca(OH)2  | Clay fraction of the Callovo-Oxfordian hard shale formation | 168 h | 120 | ― | (11 Å) TobermoriteKatoitePortlanditeGypsumCalcite | Ramírez et al. (2005) |
| pH 12.0 Ca(OH)2 | Compacted bentonite-sand mixture (contain Ca-exchanged bentonite 15 wt%, Volclay, 1.55 Mg/m3) | 2 y | 50 | Beidellization | Al-bearing C-S-HCalcite | Yokoyama et al. (2011) |
| NaOH, in the presence of portlandite (pH 12.9―13.52) | The < 1 mm fractions of bentonite (La Serrata de Níjar) | Max. 18 m | 25 | ― | SaponiteC-S-H | Sánchez et al. (2006) |
| 75 | ― | SaponiteC-S-HPhillipsite |
| 125 | ― | SaponiteC-S-H11 Å TobermoriteAnalcime |
| 200 | ― | Saponite11 Å TobermoriteGyroliteAnalcime |
| Concrete (CEM-I-SR) | Compacted bentonite (FEBEX bentonite, 1.65 g/cm3) | Max. 6.5 y | Gradient (100ºC at bottom of bentonite and ~ 40ºC at the interface) | ― | C-A-S-HCalciteAragonite | Fernández et al. (2016) |
| Portlandite in water | Bentonite / the < 2 μm fractions of bentonite (FEBEX bentonite) | 2 m | 60 | ― | C-A-S-H | Fernández et al. (2016) |
| 120 | ― | C-A-S-HAl-tobermorite (\*A sharp XRD diffraction that departs from the pure C-S-H was observed.) |
| Ordinary Portland cement (OPC) paste | Compacted bentonite (Kunigel-V1 with and without Na2CO3 admixture, 1.6×103 kg/m3) | Max. 20 m | ― | ― | CalciteC-S-HEttringite / MonosulfateZeolite or feldspar? | Nakarai et al. (2021) |
| LAC concrete installed at Mont Terri Underground Research Laboratory | Host clayey rock (Opalinus Clay: OPA) | 5 y | ― | ― | Mg-bearing smectiteMg-bearing smectite with Mg(OH)2 in the interlayerCalciteC-S-HGypsum? | Lerouge et al. (2017) |
| CEM-II cement paste/concrete installed at Tournemire Underground Research Laboratory | Host clayey rock (Tournemire argillite) | 15 y | ― | ― | C-S-HCalciteEttringiteCelestineMg-rich mineral phaseK-feldspar | Techer et al. (2012) |
| OPC cement paste installed at Tournemire Underground Research Laboratory | Host clayey rock (Tournemire argillite) | 1 y | 70 | ― | C-A-S-H11 Å Tobermorite(K-rich) PhillipsiteCalciteEttringite | Lalan et al. (2016) |
| Shotcrete concrete plug (CEM-II A-L 35.5 R cement with additions of nano-silica, polypropylene, and steel fibers, etc.) installed at Grimsel Underground Research Laboratory | Compacted bentonite (FEBEX bentonite, 1.6―1.7 g/cm3) | 13 y | 15―35 | Intercalation of Mg(OH)2 | Serpentine-like mineralEttringiteCalciteGypsumC-(A-)S-H | Fernández et al. (2017) |

**Figure legends**

**Fig. S1. Temperature and time dependency for the formation of C–(A–)S–H or tobermorite during the alkaline alteration of bentonite or clay.**

\*The previous studies on which the plots in this figure are shown in Sup Table 4. Data for which reaction temperature was not stated in the previous studies were plotted as if the reaction had occurred at 25ºC. The reaction temperature of 15–35ºC reported by Lalan et al. (2006) is plotted at 25ºC in this figure.

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