Article

Channelized CO₂-Rich Fluid Activity along a Subduction Interface in the Paleoproterozoic Wutai Complex, North China Craton

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Abstract: Greenschist facies metabasite (chlorite schist) and metasediments (banded iron formation (BIF)) in the Wutai Complex, North China Craton recorded extensive fluid activities during subduction-related metamorphism. The pervasive dolomitization in the chlorite schist and significant dolomite enrichment at the BIF–chlorite schist interface support the existence of highly channelized updip transportation of CO₂-rich hydrothermal fluids. Xenotime from the chlorite schist has U concentrations of 39–254 ppm and Th concentrations of 121–2367 ppm, with U/Th ratios of 0.11–0.62, which is typical of xenotime precipitated from circulating hydrothermal fluids. SHRIMP U–Th–Pb dating of xenotime determines a fluid activity age of 1.85 ± 0.07 Ga. The metasomatic dolomite has $\delta^{13}\text{C}_{\text{V-PDB}}$ from -4.17‰ to -3.10‰ , which is significantly lower than that of carbonates from greenschists, but similar to the fluid originated from Rayleigh fractionating decarbonation at amphibolite facies metamorphism along the regional geotherm ($\sim 15^\circ\text{C}/\text{km}$) of the Wutai Complex. The $\delta^{18}\text{O}_{\text{V-SMOW}}$ values of the dolomite (12.08‰ – 13.85‰) can also correspond to this process, considering the contribution of dehydration. Based on phase equilibrium modelling, we ascertained that the hydrothermal fluid was rich in CO₂, alkalis, and silica, with $X(\text{CO}_2)$ in the range of 0.24–0.28. All of these constraints suggest a channelized CO₂-rich fluid activity along the sediment–basite interface in a warm Paleoproterozoic subduction zone, which allowed extensive migration and sequestration of volatiles (especially carbon species) beneath the forearc.

Keywords: dolomite; C–O isotopes; fluid channelization; carbon cycle; warm subduction

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1. Introduction

Subduction zones are dynamic sites of mass and energy exchange between the Earth's interior and the surface [1–4]. The presence and movement of fluids and melts at a variety of scales and levels facilitates and governs geochemical cycles and fluid-enhanced deformation within subduction zones [5–8]. Geochemical studies [6,9,10] and numerical simulations [11] suggest that the fluid flow in subduction zones may be strongly channelized but not pervasive, under the control of the low permeability in subducting slabs, the high dihedral angles between fluid and minerals, and the negative rock volume change during prograde metamorphism [12,13]. Investigation of fluid channelization is therefore critical for the understanding of fluid fluxes and flow paths in the subduction zones [12], and sequentially, for the understanding of the material cycles of substances such as water, carbon, water-soluble salts, and abiogenic hydrocarbons. However, it is difficult to obtain detailed information (for example, the locus, scale, and orientation) about the fluid channels in a subduction zone, since they are located at a great depth or have been dismembered during exhumation and exposure.

Carbon dioxide is one of the principal volatile components in subduction zones. The atmospheric and oceanic CO₂ levels regulate the evolution of climate and life on our planet over geological time [14–17]. Carbon dioxide also buffers the pH range of ore-forming fluids to maintain elevated metal concentrations [18]. The CO₂ proportion of fluids within a subduction zone is partly controlled by the metamorphic decarbonation of the subducting slab, which shows significantly different behavior in cold and warm subduction zones [19,20]. In a warm subduction zone, the majority of CO₂ expulsion from the slab occurs beneath the forearc [7]; this would have a profound impact on the carbon cycle model and CO₂ flux estimates.

This study reports direct observations of fluid channel relics within a shallowly subducted terrane in a warm Paleoproterozoic subduction zone, which provides detailed insights into fluid fluxes and flow paths, as well as its composition, origin, and transportation behavior in a warm subduction setting.

2. Geologic Setting and Samples

2.1. Regional Geology

The Wutai complex—together with Hengshan Complex, Fuping Complex and Hutuo Group—is located in the middle segment of the Trans-North China Orogen, North China Craton (Figure 1a,b) [21]. The Fuping Complex is mainly composed of mafic granulites and late-Neoproterozoic TTG (tonalite–trondhjemite–granodiorite) gneisses [22–24], and is separated from the Wutai Complex by a ductile shear zone trending to the northeast at Longquanguan (Figure 1b). The Hengshan Complex is separated into the northern high-pressure granulite facies terrane (including late-Neoproterozoic TTG gneisses) [23,25] and the southern amphibolite facies terranes by an EW-directional ductile shear zone at Zhujiayang (Figure 1b). These metamorphic rocks recorded peak *P–T* conditions at around 12–15 kbar and 750–850 °C [26–29]. The Wutai Complex comprises metamorphic supracrustal rocks (Wutai Group) and foliated TTG gneisses (Figure 1c), typical of granite–greenstone belts. The TTGs—such as the Ekou, Chechang, Beitai, and Shifo intrusions—are distributed along the regional structural lines (Figure 1c), with emplacement ages of 2.56–2.52 Ga [30,31]. The Wutai Group is subdivided into three subgroups, including the amphibolite facies lower (Shizui) subgroup, the greenschist facies middle (Taihuai) subgroup, and the subgreenschist facies upper (Gaofan) subgroup (Figure 1c) [32]. The lower subgroup mainly contains garnet amphibolites, garnet–mica schists, and garnet orthoamphibole rocks. They recorded peak *P–T* conditions at around 9–12 kbar and 620–670 °C [29,33–35]. The amphibolite facies to granulite facies metamorphism in the Hengshan, Wutai, and Fuping areas indicates a protracted *P–T–t* evolution, including a peak stage at ~1.95 Ga, post-peak exhumation, and final slow cooling during 1.92–1.80 Ga [36–38]. There was also considerable middle-Paleoproterozoic (2.3–2.0 Ga) mafic and felsic magmatism in these areas [36]. The Hutuo Group consists of subgreenschist facies metamorphic sediments in a preceding transgressive sequence at 2.15–2.03 Ga, and a succeeding regressive sequence at 1.95–1.80 Ga [39,40].

2.2. Field Occurrence and Sample Description

The study area belongs to the middle subgroup of the Wutai Group, where greenschist facies banded iron formation (BIF), chlorite schists (altered basalts), and pillow basalts occur in a successive distribution from south to north. At the outcrop at Kangjiagou, the BIF overlies the chlorite schist (Figure 2a), and preserves its stratifications (Figure 2b). The chlorite schist has experienced extensive dolomitization and partial muscovitization, with voluminous coarse-grained saddle crystals and thin veins of dolomite (Figure 2c,d). There is significant dolomite enrichment in the BIF–chlorite-schist contact zone (Figure 3a). The pillow basalt is located in the vicinity of Taping; the pillow structure is well preserved, and does not show evidence of mineralization like the chlorite schist (Supplementary Materials, Figure S1).

Figure 1. (a) Tectonic sketch of the North China Craton. (b) Geological map showing the distribution and metamorphic grades of the Wutai, Hengshan, and Fuping complexes and the Hutuo Group. G: granulite facies; A: amphibolite facies; GS: greenschist facies; SGS: sub-greenschist facies; (c) Geological map showing the lithological units in the Wutai Complex, including the three subgroups of Wutai Group and TTG gneisses. The localities of BIF and chlorite schist (Kangjiagou, large star) and pillow basalt (Taping, small star) are also shown. The tectonic division of the North China Craton is in accordance with [21]. Metamorphic grades of each geological unit and classification of subunits in the Wutai Complex are in accordance with [36].

The dolomite-bearing chlorite schist (samples 16EK05 and 16EK06) mainly consists of chlorite and dolomite (Figure 3b), with subordinate muscovite, albite, quartz, pyrite, and chalcopyrite. Dolomite occurs in rhombic shapes with sweeping rims and obvious twinning striations; it commonly has inclusions of fine-grained quartz and albite. Chlorite occurs as aggregations, and forms the matrix together with quartz and albite. Muscovite generally occurs as individual flakes in the matrix. In addition, a small number of xenotime grains were obtained from sample 16EK06 by heavy liquid and magnetic separation, which can be used to date low-temperature geological processes [41]. The BIF mainly consists of quartz, magnetite, and dolomite in variable granularities; it is heterogeneous and distinct in magnetite-rich (sample 16EK02) and dolomite-rich (sample 17EK11) subtypes (Figure 3c). The dolomite-rich BIF also contains a significant amount of pyrite.

Figure 2. Photographs of the outcrop at Kangjiagou, Wutai Complex. (a) BIF overlies the chlorite schist. (b) BIF with stratifications. (c) Chlorite schist contains voluminous coarse-grained crystals and thin veins of dolomite. (d) Chlorite schist with both dolomitization and muscovitization (the scattered small white flakes).

Figure 3. (a) Photograph showing the dolomite enrichment in the BIF–chlorite-schist contact zone. (b) Photomicrograph of the dolomite porphyroblasts and chlorite-dominated matrix in the chlorite schist. (c) Photomicrographs of dolomite-rich and magnetite-rich subtypes of BIF. dol: dolomite; chl: chlorite; mt: magnetite.

3. Methods

3.1. Instrumental Analyses

The major and trace element compositions of the minerals were analyzed using a JEOL 8230 (manufacturer, city, state, country) electron microprobe analyzer (EMPA) and COMPex Pro102 (manufacturer, city, state, country) and Agilent 7500ce (manufacturer, city, state, country) laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS), respectively, at the Key Laboratory of Orogenic Belts and Crustal Evolution, Peking University, Beijing. On the EMPA, the acceleration voltage and beam current were 15 kV and 10 nA, respectively. The beam was 2 μm in diameter, and counting times were 10–15 s. The SPI 53 minerals standard (U.S.) was used for the quantitative analysis, and PRZ correction was performed at the final calibration stage. Other details are described in [42]. The EMPA-analyzed results and stoichiometrically calculated mineral formulas are presented in Table S1. For the LA-ICP-MS, the laser beam was 36 μm in diameter, and its frequency was 10 Hz. The USGS and Chinese National standards BHVO-2 and GSR-2 were chosen for element concentration calibration. Other details are described in [43].

Carbon–oxygen isotopes of carbonate and oxygen isotopes of silicates that were collected via microdrill from different parts of the rock samples were analyzed using a Thermo Fisher MAT-253 mass spectrometer with a GasBench II system at the Laboratory for Stable Isotope Geochemistry, Institute of Geology and Geophysics, China Academy of Science. Approximately 300 μg of carbonate powders was reacted with 100% phosphoric acid at 70 $^{\circ}\text{C}$ within a 12-mL vial tube filled with He, and the generated CO_2 gas was injected into the mass spectrometer for measurement of the isotopic compositions. Internal standard monitoring showed that the standard deviations of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ were smaller than 0.15‰ and 0.20‰, respectively. Other details are described in [44].

Oxygen isotopes of quartz, magnetite and, incidentally, dolomite were analyzed in situ by the sensitive high-resolution ion microprobe (SHRIMP) II at the Research School of Earth Sciences, Australian National University, Canberra. Data were acquired via a Cs^+ primary beam, which was focused into a spot 20–30 μm in diameter on the target surface to generate O^- secondary ions from the minerals. Other configurations of the ANU SHRIMP II for oxygen isotopic analysis are described in detail in [45]. Mineral standards of UWQ1 quartz, RSES magnetite, and NBS19 dolomite measured in the same session were used as normalizing reference materials. SHRIMP spots that were not in focus, or overlapped inclusions or adjacent minerals, were rejected. The results are presented in Supplementary Table S2.

Xenotime U–Th–Pb isotope analysis was conducted via SHRIMP at the Research School of Earth Sciences, Australian National University, Canberra. The primary O_2^- beam was focused to 5–10 μm in diameter, 6 scans of data were acquired in each analysis, and MG-1 and BS-1 xenotimes were used as standards. Other details about the analytic procedures are similar to those described in [46]. Data were reduced using the Isoplot-4.15 Excel macro [47].

3.2. Phase Equilibria Modelling and C–O Isotopes Calculations

Phase equilibria modelling was performed in the Na_2O – CaO – K_2O – FeO – MgO – Al_2O_3 – SiO_2 – H_2O – CO_2 (NCKFMASHC') system. Pseudosections were calculated using THERMOCALC 3.40 [48] with the ds62 dataset [49]. The activity models of relevant phases were the same as or degenerated from previous coding [50–52]. The fluid was assumed to be H_2O – CO_2 , and set to be excess. The normalized bulk rock composition used in the calculations is presented in Supplementary Table S3.

Oxygen isotope fractionation between minerals is temperature dependent. The equilibrium temperature (T , in Kelvin) of oxygen isotopes between quartz and magnetite was calculated using the equation $10^3 \cdot \ln\alpha_{\text{q-mt}} = 1.22 \times 10^6/T^2 + 8.22 \times 10^3/T - 4.35$ [53]. Oxygen isotopes of the water in equilibrium with dolomite and quartz were calculated using the equations $10^3 \cdot \ln\alpha_{\text{dol-water}} = 3.06 \times 10^6/T^2 - 3.24$ [54], and $10^3 \cdot \ln\alpha_{\text{q-water}} = 3.05 \times 10^6/T^2 - 2.09$ [55], respectively.

The oxygen isotopic equilibrium between different lithological samples was assessed using the $\delta^{18}\text{O}$ –GI diagram [56,57], where GI is the Garlick index defined as $(\text{O}_{\text{Si}} + 0.58\text{O}_{\text{Al}})/\text{O}_{\text{total}}$ in oxygen equivalents [58], applied to minerals or bulk rocks.

The $\delta^{18}\text{O}$ – $\delta^{13}\text{C}$ evolving trends of fluids produced during Rayleigh fractionating decarbonation processes were modelled after the equation detailed in [59]. The isotopic fractionation coefficients are cited from [60,61].

4. Results

4.1. Mineral Chemistry

Dolomite is highly stoichiometric, with Ca cations of 0.99–1.01 pfu (per formula unit); it is ferroan, and shows $X_{\text{Fe}} = \text{Fe}^{2+}/(\text{Mg} + \text{Fe}^{2+})$ of 0.37–0.44. The PAAS (post-Archaeon Australia shale)-normalized REE (rare-earth element) patterns of the dolomite (Table 1; Figure 4a) show depleted light REEs with $(\text{La}/\text{Sm})_{\text{N}}$ of 0.02–0.06, markedly positive Eu anomalies with $(\text{Eu}/\text{Eu}^*)_{\text{N}}$ of 9–27, and slightly negative Y anomalies with $(\text{Y}/\text{Y}^*)_{\text{N}}$ of 0.6–0.9. It has particular Sr and Pb concentrations of 142–276 ppm and 8.6–11.8 ppm, respectively. Chlorite shows X_{Fe} of 0.52–0.55, and has Si contents of 2.60–2.77 pfu, classified as ripidolite [62,63]. Muscovite shows $X_{\text{Na}} = \text{Na}/(\text{Na} + \text{K})$ of 0.13–0.20 and $\text{Al}_{\text{M2}} = \text{Al}^{\text{VI}}/(\text{Al}^{\text{VI}} + \text{Mg} + \text{Fe}^{2+})$ of 0.91–0.93.

Table 1. Trace elements concentrations (ppm) of dolomite from the chlorite schist.

Element	dol-1	dol-2	dol-3	dol-4	dol-5	Element	dol-1	dol-2	dol-3	dol-4	dol-5
Sc	27.71	26.5	21.41	21.87	20.29	Gd	0.176	0.315	0.1495	0.197	0.64
Rb	0.0091	0.0095	0.0103	0.0088	0.0102	Tb	0.0219	0.0538	0.0195	0.0319	0.1059
Sr	143.11	141.74	150.29	165.68	275.99	Dy	0.1373	0.268	0.1182	0.1655	0.495
Y	0.74	0.939	0.564	0.513	1.75	Ho	0.0326	0.0508	0.0238	0.0304	0.0791
Zr	29.23	0.2392	23.28	0.32	0.004	Er	0.1103	0.1276	0.0857	0.0635	0.1952
Nb	0.0047	0.297	0.0033	0.0027	0.0031	Tm	0.0292	0.02	0.0193	0.0129	0.0232
Ba	0.069	0.114	0.0741	0.1066	0.209	Yb	0.228	0.1429	0.1876	0.1009	0.262
La	0.0231	0.0287	0.0204	0.061	0.085	Lu	0.0538	0.0326	0.0406	0.0244	0.0435
Ce	0.0872	0.1305	0.075	0.1438	0.321	Hf	0.927	0.0148	0.641	0.0082	0.0064
Pr	0.022	0.0363	0.0137	0.0317	0.0707	Ta	0.0024	0.0151	0.0025	0.0019	0.0019
Nd	0.1741	0.308	0.1151	0.241	0.626	Pb	11.777	11.217	10.639	9.6	8.62
Sm	0.0997	0.234	0.0847	0.1487	0.452	Th	0.0149	0.0056	0.015	0.0033	0.0041
Eu	0.571	0.522	0.537	0.982	1.027	U	0.0269	0.0096	0.0155	0.0025	0.0028

Figure 4. (a) Post-Archaeon Australia shale (PAAS)-normalized REE patterns of dolomite from the chlorite schist (squares). The representative sedimentary dolomite is also shown (diamonds, data from [64]). (b) MORB-normalized trace element patterns of dolomite from the chlorite schist (squares). Experimentally determined subduction zone (SZ) fluids are also shown (diamonds: Cl-present; triangles: Cl-free; data from [65]). Elements are plotted in order of decreasing compatibility, in accordance with [66].

4.2. C–O Isotopes

The porphyroblastic dolomite from the chlorite schist sample 16EK05 has $\delta^{13}\text{C}_{\text{V-PDB}}$ from -4.17‰ to -3.90‰ and $\delta^{18}\text{O}_{\text{V-SMOW}}$ of $13.34\text{--}13.59\text{‰}$. Similarly, dolomite from sample 16EK06 has $\delta^{13}\text{C}_{\text{V-PDB}}$ from -3.83‰ to -3.10‰ and $\delta^{18}\text{O}_{\text{V-SMOW}}$ of $12.08\text{--}13.85\text{‰}$. The chlorite-dominated silicate matrix from sample 16EK05 has $\delta^{18}\text{O}_{\text{V-SMOW}}$ of 5.64‰ , while that from sample 16EK06 has $\delta^{18}\text{O}_{\text{V-SMOW}}$ of 4.63‰ (Table 2).

Table 2. C–O isotopes (‰) of porphyroblastic dolomite and silicate matrix in the chlorite schist.

Materials	Samples	$\delta^{13}\text{C}_{\text{V-PDB}}$	$\delta^{18}\text{O}_{\text{V-PDB}}$	$\delta^{18}\text{O}_{\text{V-SMOW}}$
Dolomite	16EK05	−3.90	−16.80	13.59
		−3.99	−16.97	13.42
		−4.17	−17.04	13.34
	16EK06	−3.10	−18.27	12.08
		−3.83	−16.55	13.85
	17EK11 ^a	−3.82	−18.02	12.33
	Kang-2 ^b	−4.28	−	10.94
		−4.39	−	11.62
Matrix	16EK05	−	−	5.64
	16EK06	−	−	4.63

^a Dolomite-rich BIF. ^b Cited from [67].

Quartz from the BIF sample 16EK02 has $\delta^{18}\text{O}_{\text{V-SMOW}}$ of $12.01\text{--}12.95\text{‰}$, with a weighted mean of $12.5\text{‰} \pm 0.1\text{‰}$, while that from sample 17EK11 has $\delta^{18}\text{O}_{\text{V-SMOW}}$ of $11.70\text{--}12.97\text{‰}$, with a weighted mean of $12.3\text{‰} \pm 0.2\text{‰}$ (Table 3). Magnetite from sample 16EK02 has $\delta^{18}\text{O}_{\text{V-SMOW}}$ of $-6.03\text{--}0.18\text{‰}$, with a weighted mean of $-2.8\text{‰} \pm 0.7\text{‰}$, while that from sample 17EK11 has $\delta^{18}\text{O}_{\text{V-SMOW}}$ of $-3.22\text{--}2.51\text{‰}$, with a weighted mean of $-0.6\text{‰} \pm 1.9\text{‰}$ (Table 3). Dolomite from BIF sample 17EK11 has $\delta^{13}\text{C}_{\text{V-PDB}}$ and $\delta^{18}\text{O}_{\text{V-SMOW}}$ values similar to those of the chlorite schist, which are -3.82‰ and 12.33‰ , respectively.

Table 3. Oxygen isotopes ($\delta^{18}\text{O}_{\text{V-SMOW}}$, ‰) of dolomite (dol), quartz (qz), and magnetite (mt) from the chlorite schist and BIF (analyzed by SHRIMP).

Minerals	Samples	Ranges		Weighted Mean		Count
		Min.	Max.	Mean	1 σ	
dol	16EK05 ^a	11.50	12.08	11.84	0.08	20
	16EK06 ^a	11.29	12.01	11.67	0.08	27
qz	16EK02	12.01	12.95	12.5	0.1	27
	17EK11	11.70	12.97	12.3	0.2	19
mt	16EK02	−6.03	0.18	−2.8	0.7	27
	17EK11 ^a	−3.22	2.51	−0.6	1.9	8

^a not involved in discussion.

4.3. Date and U–Th Contents of Xenotime

Xenotime shows $^{206}\text{Pb}/^{238}\text{U}$ dates from 1753 ± 33 Ma to 1916 ± 29 Ma, with a weighted mean of 1852 ± 69 Ma and a lower intercept of 1848 ± 66 Ma (Figure 6a). Xenotime has U contents of 39–254 ppm and Th contents of 121–2367 ppm, with U/Th ratios of 0.11–0.62 (Table 4).

Table 4. Xenotime U–Pb isotopic data and corrected ages.

No.	Th (ppm)	U (ppm)	U/Th	Total Isotopic Ratios				²⁰⁴ Pb Corrected Ages (Ma)			
				²³⁸ U/ ²⁰⁶ Pb	sd. %	²⁰⁷ Pb/ ²⁰⁶ Pb	sd. %	²⁰⁶ Pb/ ²³⁸ U	1σ sd.	²⁰⁷ Pb/ ²⁰⁶ Pb	1σ sd.
xen1.1	121	39	0.32	3.067	3.65	0.1177	4.24	1782	61	1567	256
xen1.2	212	51	0.24	2.882	3.71	0.1360	4.05	1895	63	1999	158
xen2.1	380	235	0.62	2.877	1.76	0.1166	1.39	1916	29	1848	37
xen3.1	2367	254	0.11	2.940	1.74	0.1150	1.35	1886	29	1869	27
xen3.2	804	132	0.16	3.156	2.09	0.1161	2.04	1753	33	1696	88
xen3.3	1138	155	0.14	3.010	1.96	0.1097	1.89	1833	32	1643	72

Note: sd—standard deviation.

4.4. Pseudosections

The T – $X(\text{CO}_2)$ ($X(\text{CO}_2) = \text{CO}_2/(\text{H}_2\text{O} + \text{CO}_2)$ in moles) pseudosection (Figure 5a) shows that the carbonate phase varies from calcite and dolomite to siderite as $X(\text{CO}_2)$ increases. The observed mineral assemblage dominated by dolomite and chlorite in the chlorite schist sample (Figure 3b) indicates a small range of the systemic CO_2 concentration, with $X(\text{CO}_2)$ around 0.24–0.28.

Figure 5. T – $X(\text{CO}_2)$ (a) and P – T (b) pseudosections calculated for the dolomite-bearing chlorite schist. They are shaded with increasing color depth for the fields of increasing degrees of freedom. The observed mineral assemblage in the sample is highlighted. $X(\text{CO}_2) = \text{CO}_2/(\text{H}_2\text{O} + \text{CO}_2)$ in moles. q: quartz; pl: plagioclase; mu: muscovite; chl: chlorite; dol: dolomite; sid: siderite; cc: calcite; bi: biotite.

The P – T pseudosection at an $X(\text{CO}_2)$ of 0.25 (Figure 5b) shows that the carbonate varies from siderite and dolomite to calcite, while the muscovite is transformed to biotite with rising temperatures. The observed mineral assemblage in the chlorite schist (dol + chl + q + ab + mu) defines a narrow-banded P – T field with a positive slope; it constrains temperatures around 260–400 °C at the variable pressures of 1–6 kbar.

4.5. Oxygen Isotopic Equilibrium

Quartz and magnetite in the BIF reached oxygen isotopic equilibrium at temperatures of 246–282 °C; this temperature range is similar to that recorded by chlorite in the chlorite schist (234–250 °C; Table S1) [73–75]. Oxygen isotopes ($\delta^{18}\text{O}_{\text{V-SMOW}}$) of H_2O in equilibrium with dolomite in the chlorite schist and quartz in the BIF were estimated to be 3.7–5.4‰ and 3.5–4.4‰, respectively. These similar values suggest a good oxygen isotopic equilibrium between the chlorite schist and BIF samples, which can also be supported by the $\delta^{18}\text{O}$ –GI

diagram (Figure S2). Therefore, H₂O in the hydrothermal fluid should have $\delta^{18}\text{O}_{\text{V-SMOW}}$ around 3.5–5.4‰, consistent with a metamorphic fluid [76].

5. Discussion

5.1. Hydrothermal Fluid Activity

5.1.1. Evidence for Fluid Activity

Dolomite occurs in both dolomite-bearing chlorite schist and BIF samples; its saddle texture—especially the turbid inclusion-rich core and the clean sweeping rim (Figure 3b)—indicates a hydrothermal genesis [77–81]. This is different from sedimentary and burial dolomite that commonly occurs in sucrosic, fibrous, or oolitic textures [82–84]. In terms of composition, the highly stoichiometric dolomite is only commonplace as metamorphic or metasomatic units, whereas the sedimentary dolomite is usually nonstoichiometric, with excess Ca cations [85]; it requires facilitative fluid flow for a sufficient supply of Mg–Fe²⁺ cations [85]. Moreover, the REE patterns of the investigated dolomite display marked inconformity with the typical pattern of sedimentary dolomite (Figure 4a) [64]. The characteristic light REE depletion of the investigated dolomite is consistent with the mafic rocks modified by silica-diluent metasomatism [86]. Furthermore, carbon isotopes of the dolomite ($\delta^{13}\text{C}_{\text{V-PDB}}$ from −4.17‰ to −3.10‰) can distinguish it from marine carbonate (typically 0–4‰) [85]. Oxygen isotopes of the dolomite ($\delta^{18}\text{O}_{\text{V-SMOW}} = 12.08\text{--}13.85\text{‰}$) can also distinguish it from the igneous carbonatite and sedimentary carbonates, which have $\delta^{18}\text{O}_{\text{V-SMOW}}$ of 6–10‰ and 15–30‰, respectively [44,87]. In a nutshell, the combined evidence from texture, major and trace compositions, and C–O isotopes of the dolomite in this study reflects unambiguous hydrothermal fluid activity.

Xenotime generally forms in fractionated igneous rocks such as pegmatites, and can also form during diagenesis, hydrothermal mineralization, and metamorphism. The U–Th concentrations of xenotime were linked to its formation environments [68]. Xenotime from the dolomite-bearing chlorite schist has significantly lower U concentrations (39–254 ppm) and U/Th ratios (0.11–0.62); it exclusively overlaps the hydrothermal xenotime from iron and gold deposits (Figure 6b) [68–72]. Such xenotime is associated with low-salinity hydrothermal fluids, and tends to have the lowest U content (<100 ppm) and U/Th ratio (<4) among xenotimes of diverse origins [68]. Therefore, the U–Th concentrations of xenotime in the dolomite-bearing chlorite schist can also indicate hydrothermal fluid activity. Moreover, the precipitation of xenotime during the circulation of hydrothermal fluids was probably responsible for the negative Y anomalies in the dolomite.

5.1.2. Fluid Compositions

The chemical composition of the hydrothermal fluids can be derived from comparison between the metamorphic pillow basalt and the hydrothermally altered metabasalt. The metamorphic pillow basalt, which lacks mineral and textural indications for hydrothermal metasomatism, commonly contains fine-grained quartz, albite, chlorite, and epidote (Figure S1). In contrast, the dolomite-bearing chlorite schist, which underwent hydrothermal metasomatism, contains quartz, albite, chlorite aggregates, dolomite porphyroblasts, and muscovite (Figures 2c,d and 3b). The substantial dolomitization and muscovitization in the metasomatic chlorite schist suggest that the hydrothermal fluid is rich in solutes of CO₂ and alkalis (Na and K in general).

It was widely proposed that immiscibility occurs between carbonic and saline fluids due to their different densities and wettability [88–92]. Nevertheless, silica dilution can mutually reinforce the miscibility and solubility of CO₂ and alkalis in the hydrothermal fluid. For instance, the silica salting-in effect was proposed long ago, which invoked that the solute alkalis and silica can produce a hydrous complex (Na, K)HSiO₃·H₂O [93]. Silica would also solve strongly into a concentrated salt solution in metamorphic and metasomatic processes [94]. Recent experiments suggest that silicate dissolution boosts the CO₂ concentrations in subduction fluids, probably associated with the formation of

complexes containing Si–O–C bonds [95]. Therefore, the hydrothermal fluid is likely also rich in solutes of SiO₂.

The hydrothermally metasomatic process could be described using the following reaction: $3(\text{Mg, Fe})_4\text{Al}_4\text{Si}_2\text{O}_{10}(\text{OH})_8^{\text{chl}} + 6\text{Ca}_2\text{Al}_3\text{Si}_3\text{O}_{12}(\text{OH})^{\text{ep}} + 6\text{SiO}_2^{\text{aq}} + 24\text{CO}_2^{\text{aq}} + 10(\text{Na, K})^{+\text{aq}} = 10(\text{Na, K})\text{Al}_3\text{Si}_3\text{O}_{10}(\text{OH})_2^{\text{mu}} + 12\text{Ca}(\text{Mg, Fe})(\text{CO}_3)_2^{\text{dol}} + 10\text{H}^{+\text{aq}}$. Through this reaction, the greenschist facies metabasalt was metasomatized by the hydrothermal fluid to form dolomite and muscovite, exhausting the epidote that formed in the metamorphic stage. On the other hand, the fluid interaction to the metabasalt would result in an enrichment of alkalis and silica, as mentioned above, and in particular, the CO₂-rich fluid may also carry leached gold in, as some low-grade gold enrichment occurs in the carbonated chlorite schist [67].

Figure 6. (a) Backscattered electron (BSE) images of representative xenotime grains. (b) Energy-dispersive spectrometer (EDS) semiquantitative analyses of xenotime. (c) Tera–Wasserburg concordia diagram for the xenotime dates. (d) U/Th–U diagram for different genetic types of xenotime. The shadowed fields summarize the igneous (I), metamorphic (M), diagenetic (D), and hydrothermal (H) xenotimes (data from [68]), with hydrothermal xenotime from iron (squares; data were collected from [69,70]) and gold (diamonds; data were collected from [71,72]) deposits highlighted. The circles are xenotime from the dolomite-bearing chlorite schist in this study.

5.1.3. Origin of the Fluid

The xenotime dating acquires a fluid activity age of 1.85 ± 0.07 Ga, which is synchronous with the regional metamorphic ages of 1.95–1.78 Ga [36,37]. This suggests that the activity of the hydrothermal fluid is related to the regional metamorphic or tectonic events.

The C–O isotopic systematics of metasomatic minerals can be used to constrain the source of the hydrothermal fluid [96]. In the investigated samples, dolomite from the hydrothermally metasomatic chlorite schist and BIF had $\delta^{18}\text{O}_{\text{V-SMOW}}$ of 12.08–13.85‰ and $\delta^{13}\text{C}_{\text{V-PDB}}$ of −4.17–−3.10‰ (Table 2). For such C–O isotopic characteristics, a fluid source of devolatilized metasedimentary rocks is unlikely, given that hydrothermal fluid from this source generally forms carbonates with much heavier oxygen isotopes ($\delta^{18}\text{O}_{\text{V-SMOW}}$ around 17–27‰) [6,10,97]. A fluid source of devolatilized metabasite is more likely, as fluid derived from such a source precipitates carbonates with a large $\delta^{18}\text{O}_{\text{V-SMOW}}$ range of about 8–22‰ [5,96,98], which covers the measured dolomite $\delta^{18}\text{O}_{\text{V-SMOW}}$ values.

To confirm the origin of the fluid further, we compare our data with C–O isotopes of high-pressure veins from published literature, which are thought to represent the conduits of fluid that internally derives from the host rocks during metamorphic devolatilization [10,57,98–102]. The C–O isotopes of vein carbonates in metabasites were compiled in Figure 7 in order to trace the fluids sourced from different facies of metabasite. We did not classify the collected isotopic data by their mineral types, because the C and O isotopes among dolomite, calcite, and siderite are almost identical at 400–600 °C, considering that the isotopic fractionation between these phases is very minor (near 0.5‰) [98,103]. Plots of the carbonates' C–O isotopes in this study are overlapped with the carbonate minerals occurring in amphibolites, while distinct from those in greenschists (Figure 7). We modelled the C–O isotopic Rayleigh fractionation during decarbonation without (Figure 7a) or with (Figure 7b) the contribution of dehydration in the process of metamorphic devolatilization in carbonated seafloor basalt; Our results show that a coupled decarbonation and dehydration process with decreasing $X(\text{CO}_2)$ of the released fluids at ~650 °C can well match the analyzed C–O isotopes of dolomite in the chlorite schist (Figure 7b). Moreover, the oxygen isotopes of vein quartz also show inconsistency among different facies of metabasite; for instance, vein quartz in blueschist has $\delta^{18}\text{O}_{\text{V-SMOW}}$ around 17–18‰, whereas that in amphibolite has $\delta^{18}\text{O}_{\text{V-SMOW}}$ around 12–13‰ [5]. The $\delta^{18}\text{O}_{\text{V-SMOW}}$ of quartz (11.70–12.97‰) from the metasomatic BIF also overlaps the $\delta^{18}\text{O}_{\text{V-SMOW}}$ range of amphibolite. All of these facts support the notion that the hydrothermal fluid isotopically in equilibrium with the dolomite and quartz analyzed in this study originated from source rocks of amphibolite facies. This inference is reasonable in terms of volatile supply, because amphibolite facies metamorphism generally produces abundant CO_2 – H_2O fluids through prograde chlorite dehydration and dolomite decarbonation [5,104,105]. The univariant reaction results in a continuous CO_2 enrichment with decreasing pressure (Figure 8) [106]. The estimated $X(\text{CO}_2)$ around 0.24–0.28 is obtained at 12–13 kbar and ~660 °C, which is consistent with the prograde amphibolitization P – T conditions of the metabasites in the Wutai Complex (Figure 8); this could also be supported by the vein calcite occurring in the garnet amphibolite from the Wutai Complex [29]. Moreover, the alkali contents in the hydrothermal fluid may be enriched by leaching the TTGs and metapelites, through the following reaction: $3(\text{Na}, \text{K})\text{AlSi}_3\text{O}_8 + 2\text{H}^+ = (\text{Na}, \text{K})\text{Al}_3\text{Si}_3\text{O}_{10}(\text{OH})_2 + 6\text{SiO}_2 + 2(\text{Na}, \text{K})^+$ [107,108].

Figure 7. The $\delta^{18}\text{O}$ – $\delta^{13}\text{C}$ variation diagrams for vein carbonates in metabasites of greenschist facies and amphibolite facies, which represent the $\delta^{18}\text{O}$ – $\delta^{13}\text{C}$ values of metamorphic fluids in each metamorphic facies. The $\delta^{18}\text{O}$ – $\delta^{13}\text{C}$ data of dolomite from the chlorite schist in this study and in previous literature [67] are plotted for comparison. The modelled $\delta^{18}\text{O}$ – $\delta^{13}\text{C}$ evolving trends of fluids produced in Rayleigh fractionating decarbonation processes are also shown, without (a) or with (b) the contribution of dehydration. Calibrations along the curves represent the fraction of carbonate that remained in solid phases. The $\delta^{18}\text{O}$ – $\delta^{13}\text{C}$ data were collected from [5,98,109,110]. The $\delta^{18}\text{O}$ of H_2O released from metabasalt adopted here is ~9.5‰ [111]. CSB: carbonated seafloor basalt.

Figure 8. Phase diagram showing the P – T paths (solid curves with arrows) and peak P – T condition for the metabasites in the Wutai Complex (Z99, [33]; Q15, [35]; QW16, [29]). This figure also shows: (1) experimentally determined phase relationships for H_2O -saturated MORB, including the rock's solidus and the stability ranges of garnet, chlorite, zoisite, and lawsonite (solid curves) [104]; (2) calculated devolatilization reaction (dashed curve with diamonds), carbonates (carb) $\pm$ amphibolite (amp) = diopside (di) + fluid [106], labeled with $X(CO_2)$ in the resultant fluid along the univariate line ($C\ 0.5$, $X(CO_2) = 0.5$); (3) the peak metamorphic P – T conditions (ellipses) of the typical warm subduction complexes Cuba and Catalina [112–114], and that of the Hengshan Complex [26–29]; and (4) the ancient (2.7–0.8 Ga) subduction P – T range (polygonal field labeled with AS) [115,116] and the oceanic slab-top P – T paths representative of Archean examples (dashed curves with arrows) [117,118].

As mentioned above, the fluid derived from devolatilized amphibolite has precipitated dolomite in the chlorite schist at shallower levels after transportation from amphibolite facies' depth. This implies that the fluid ascended through a channel connecting the deep and shallow levels of a thickened crust. When considering the regional geotherm ($\sim 15^\circ C/km$; Figure 8) [29,37], we may infer that the fluid channel occurred either in an orogenic belt or a warm subduction zone. Among these two geotectonic settings, we prefer the latter based on the following reasons: (1) The CO_2 -, alkali-, and silica-enriched hydrothermal fluid composition shows high uniformity with the high-pressure fluids related to subducted oceanic crust, which are relatively diluent aqueous solutions with dominant solutes of Si, Al, alkali elements, and sometimes CO_2 [9,66,99,106,112,119]. The present fluid does not show remarkable enrichment of Al, which should be ascribed to the virtual insolubility of Al at lower pressures [66]—in other words, the Al component is likely to be precipitated in relatively deeper rocks in the subduction channel. On the other hand, the trace element patterns of dolomite in the chlorite schist exhibit variation trends fairly similar to those of the experimentally constrained subduction zone fluids—especially the fluid with the presence of Cl anions (Figure 4b) [65,66]. (2) Plenty of rocks in the Wutai Group have protoliths typical of altered oceanic crustal materials—for instance, the garnet–orthoamphibole rock [35,120] and equivalent chlorite schist, the pillow basalt with microbial alteration textures [121], the volcanogenic massive sulfides (VMS) [122,123], and the epidosite with extremely low $\delta^{18}O$ values (our unpublished data). (3) The metamorphic peak P – T conditions of the Wutai and Hengshan complexes lie along the oceanic slab-top P – T path representative of early warm subduction (Figure 8) [117,118]—in particular, that of Hengshan, falling exactly on the ancient (2.7–0.8 Ga) subduction P – T ranges (Figure 8) [115,116]. The Wutai and

Hengshan metamorphic complexes share similar geothermal gradients with the typical warm subduction complexes represented by Catalina and Cuba (Figure 8) [112–114].

5.2. Geological Implications

Generally, most of the pore fluid in subducting slabs is expelled at shallow levels (<15 km) of the subduction channel, and some of the fluid bonded in mineral crystals is released during devolatilization, enters the overlying mantle wedge, and contributes to arc magmatism. These fluids can escape to the surface through venting at the trench seafloor or arc volcanos [5,124]. Another significant fraction of fluid will be retained in more deeply subducted slabs, and can be stored or redistributed in deeper mantle [5,124]. In this study, the greenschist facies metamorphic terrane, including metabasite (the chlorite schist) and BIF, was metasomatized by hydrothermal fluid that was generated from the devolatilization of amphibolite facies rocks in a warm subduction zone. This suggests that there was an updip flow of fluids along the subduction channel at a 50-km-shallower level (Figure 9), which means that a substantial part of the devolatilized fluids in the subducting slab would return towards the surface and be immobilized in shallow levels. For instance, these fluids can penetrate into shallower rocks and lead to reaction and precipitation of silicate and/or carbonates, which in turn reduces trace element solubility and, hence, precipitates trace-element-rich minerals [112,125]. Dolomite and xenotime in the present samples should form through this mechanism. The incoming rocks with earlier absorbed volatiles—such as the dolomite-bearing chlorite schist—would regenerate the fluid at relevant depths. This ongoing cycle could keep efficient volatile sequestration and enrichment beneath the forearc.

On the other hand, petrologic observations do not indicate large-scale fluid flow in the regional outcrops, which suggests that the fluid flow was in low flux or highly channelized. Numerical simulation shows that the lithological boundaries are mechanically weak, cause enhanced permeability, and facilitate fluid flow [11,126]. In this study, the hydrothermally metasomatic zone lies subparallel to the BIF and chlorite schist boundary (Figure 2a), which represents the interface between altered upper oceanic crust and marine sediments. The fluid-derived dolomite is enriched at the BIF–chlorite-schist contact zone (Figure 3a). These observations indicate that most fluid migrates along the sediment–metabasite (BIF–chlorite-schist) interface within the subducting slab by channelization (Figure 9), rather than by upward flow into the leading edge of the forearc by simple buoyancy drive.

Figure 9. A conceptual schematic illustrating the channelized fluid's up-dip flow along the sediment–basite interface beneath the leading edge of the forearc in a warm subduction zone. The lithological structure of the subducted slab is modified from [127], and the structure parameters of the hot subduction zone—including slab depth, dehydration loci, and metamorphic facies—follow the numerical simulation results in [128]. The bold arrows represent the fluid flow. The BIF, chlorite schist, garnet amphibolite (GA), and garnet–orthoamphibole rock (GOR) in the Wutai area are labeled at the relevant positions.

5.2.1. Implications for the Carbon Cycle

Subduction zones control the exchange of materials between the Earth's interior and surface [3,4]; they play a key role in the carbon cycle. The most critical carbon fluxes in subduction zones are carbonate-bearing rocks sunk into the deep mantle and CO₂-bearing fluids returned to the atmosphere by metamorphic and volcanic degassing [14,115,129,130]. Nevertheless, the aforementioned updip flow of fluids along the subduction channel has the potential to transport carbon to the near-surface level (<50 km) in forearc position (Figure 9). For example, the CO₂-rich fluid in this study transported carbon from the amphibolite facies metamorphic oceanic crust to much shallower greenschist facies terranes, and sequestered carbon at this level by dolomitization (Figure 9). This can explain why there is no significant transfer of carbon from the footwall into the hanging wall at depths of less than 60–70 km in the subduction zone [131].

The updip carbon flux along the subduction channel at depths of <50 km depends on the geotherm of the subduction zone. Due to the formation and wide stabilization of magnesite–siderite phase carbonate along the low geotherm, metamorphic decarbonation in cold subduction zones is negligible [19,20,132], and only limited carbon (below ~2000 ppm) can be transferred through aqueous fluid solution [131]. In contrast, metamorphic decarbonation in warm subduction zones is remarkable [19,20]; during warm subduction, oceanic slabs experience almost complete decarbonation beneath the forearc, with no further carbon release occurring at or beyond sub-arc depths [7]. In the case of the Wutai Complex, voluminous CO₂ mainly resulted from dolomite or calcite decomposition in the presence of H₂O generated by chlorite or actinolite breakdown. This CO₂ would backflow and accumulate, forming a reservoir by carbonation in the shallow levels of the subduction channel (Figure 9). This carbon reservoir, as well as the associated ores, is only temporary storage on a geological timescale, since it is easily relocated to the surface by exhumation. In a further perspective, the observed C–H–O fluids' activity may have significance for the exploration of abiogenic hydrocarbons in basins related to warm subduction fluid transportation and transformation, which has become a prospective energy solution [95,133].

5.2.2. Implications for Subduction Lubrication

The lubricating effects in the subduction channel play an important role throughout subduction channel processes [134,135]. For instance, mechanical analysis suggested that incoming unconsolidated sediments in the subduction channel led to a much lower effective friction [136,137]. This is because the pore fluids and weak phyllosilicates in sediments can efficiently lower the shear strength [135,138]. This study confirmed an updip flow of fluids along the subduction channel at depths of <50 km (Figure 9), which would permeate into the subducting rocks and reduce their material strength. For example, the hydrothermally metasomatic dolomite-bearing rocks in this study are apparently softer and weaker than dolomite-free lithologies. Subduction channels should therefore be lubricated by not only the downgoing sediments, but also the backflowing fluids. In particular, the backflowing fluids can soften and lubricate the relatively lower layers in the subducting slab sequence (e.g., the metabasalt and the metagabbro) at depths of <50 km.

As reviewed in [139], the subducted slab materials are exhumed from preferential depths of ~25–35 km and ~70–80 km. The 25–35-km-deep preferential exhumation was attributed to the fluctuation of the deformation mechanism between friction and viscous flow [139], which is commonly envisioned as a result of fluctuations in fluid pressure [140,141]. The updip flow of fluids along the subduction channel would contribute to these fluctuations. Moreover, the fluid transfer and precipitation of pore-filling minerals such as carbonates and silica can change the permeability of rocks [139,142], which would also contribute to the switch between weakening and strengthening of subduction channel rocks.

Supplementary Materials: The following are available online at <https://www.mdpi.com/article/10.3390/min11070748/s1>: Figure S1: Pillow basalt petrography; Figure S2: The $\delta^{18}\text{O}$ –GI diagram; Table S1: EMP analyses for minerals in the chlorite schist; Table S2: SHRIMP oxygen isotope analyses for minerals from the BIF and chlorite schist; Table S3: Bulk rock composition of the chlorite schist.

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