

P-T-fluid evolution of retrogressed pelitic granulite from the Limpopo Complex, South Africa

Tatsuya Koizumi^{1*}, Toshiaki Tsunogae¹

¹Univ. Tsukuba

Hydration of granulites and formation amphibolite-facies mineral assemblages is a common process in retrogressed high-grade metamorphic terranes worldwide. Here we report new petrological data of hydrated pelitic granulite from the Southern Marginal Zone (SMZ) of the Neoproterozoic Limpopo Complex in South Africa, and discuss P-T-fluid evolution based on pseudosection analysis. The pelitic granulite has a mineral assemblage of garnet + biotite + orthopyroxene + cordierite + quartz + K-feldspar + plagioclase, which is regarded as a product of decompression after the peak M1 metamorphism. The application of mineral equilibrium modelling in NCKFMASH system yields a P-T range of 750-830C/6-8.5 kbar and molar H₂O content in the rock (M(H₂O)) of 0.5-3 mol.% for the assemblage. The orthopyroxene is now totally surrounded by retrograde anthophyllite corona formed by significant increase of H₂O activity at 750-790C/6-8.5 kbar and M(H₂O) >4 mol.%. Kyanite + anthophyllite + quartz assemblage replacing cordierite was formed at consistent M(H₂O) (>7 mol.%) but slightly lower temperature of 650-700C/6.5-7.5 kbar. Such a significant increase in H₂O activity is possibly related to fluid infiltration along the Hout River Shear Zone, which marks the terrane boundary between the high-grade Limpopo SMZ and low-grade Kaapvaal Craton.

Keywords: granulite facies, hydration reaction, pseudosection, metamorphic fluid

A geochemical constraint on the formation process of a manganese carbonate nodule in the siliceous mudstone of the Juras

Ryoichi Nakada^{1*}, Takaaki Shirai², Satoshi Takahashi³, Noritoshi Suzuki², Kazuhiro Ogawa², Yoshio Takahashi¹

¹Hiroshima Univ., ²Tohoku Univ., ³Univ. of Tokyo

Manganese (Mn) carbonate nodules, which are different from seafloor Mn nodules mainly composed of MnO₂, are occasionally embedded as a lens shape in the Jurassic accretionary complexes such as the Tamba-Mino-Ashio Belt in Japan. The interpretation of the formation process of Mn carbonate is still controversial, namely whether the Mn carbonate was formed primarily or secondarily. The optical observation of thin sections shows that Mn carbonate nodules are comprised with abraded grains of rhodochrosite spherule with radiolarians and are sedimentarily embedded in siliceous mudstone. Microfossil radiolarians from the Mn carbonate nodules and the host red siliceous mudstone are dated as the Bajocian (170.3 ? 168.3 million years ago), but radiolarians in the nodules are somewhat older than those in the host red siliceous mudstone. In this study, geochemical analyses focusing on the rare earth element (REE) were performed to unlock the formation process of Mn carbonate nodules in the Tamba-Mino-Ashio Belt.

Our analysis using the X-ray absorption near-edge structure on Ce shows dominance of trivalent Ce at present, despite of a positive Ce anomaly in the PAAS-normalized REE pattern of Mn carbonate. The REE adsorption experiment on synthesized MnCO₃ does not show any distinctive positive Ce anomaly and a thermodynamic calculation suggests the possible coexistence of authigenic rhodochrosite and spontaneous oxidation of Ce. The leaching experiment that can selectively decompose carbonate phase demonstrated no Ce anomaly in the carbonate phase of Mn carbonate and poor contribution to the bulk REE concentration. The most plausible account of all the observational and experimental results is that rhodochrosite grains were primarily formed on the depositional site and subsequently transferred to the different site where siliceous mudstone was deposited.

Keywords: manganese carbonate, rare earth element, radiolarian, XAFS

Chronology and isotope study for Cretaceous and Paleogene Granitic Rocks SW Japan

Kazuya Iida^{1*}, Iwamori Hikaru¹, Park Taeho², Orihashi Yuji³, Tanimizu Masaharu⁴, Yong-Joo Jwa⁵, Sung-Tack Kwon⁶, Tohru Danhara⁷, Hideki Iwano⁷

¹Tokyo Institute of Technology, ²Eichi, ³Earthquake Research Institute, ⁴JAMSTEC, ⁵Gyeongsang Nat'l University, ⁶University of Yonsei, ⁷Kyoto Fission-Track

We especially focus on (1)spatial-temporal variation of granitic rock, (2) temporal variation of isotopic signature and whole rock chemistry and (3) tectonic and dynamic setting that caused the observed spatial-temporal variation and provided heat for the melt generation, based on the U-Pb zircon age, whole rock chemistry and Sr isotope ratio.

U-Pb zircon age determinations using LA-ICPMS was performed on total 81 rock samples. The obtained age ranges from 95 Ma to 30 Ma, with a possible temporal gap between 60 Ma and 50 Ma. During 95-60 Ma, the systematic migration of granitoid magmatism from the south to the north occurred. We also compile temporal variation of petrological signatures from literature. As a result, we observed (1) initial ratio of Sr isotopes ($^{87}\text{Sr}/^{86}\text{Sr}$) decreased from enriched characters (0.7090-0.7065) to depleted ones (0.7065-0.7050), and (2) rock types of granitoid changed from ilmenite-series to magnetite-series.

In this study, we also conduct Sr and Pb isotope initial ratio and whole rock chemistry of dated granitic samples. Based on these results, we discuss the origin of these variations and origin of granitic rocks in the SW Japan.

Petrologic study of radioactive minerals in pegmatites in Cretaceous granitoids from Setouchi, Inner Zone of SW Japan

Kei Sato^{1*}, MINAKAWA, Tetsuo², KATO, Takenori¹, MAKI, Kenshi³, IWANO, Hideki⁴, HIRATA, Takafumi³, SUZUKI, Kazuhiro¹

¹Center for Chronological Research, Nagoya Univ., ²Graduate School of Science and Engineering, Ehime Univ., ³Graduate School of Science, Kyoto Univ., ⁴Kyoto Fission-Track Co., Ltd.

In this study, radioactive minerals from three localities of pegmatite deposits in the Setouchi province, which belongs to the Inner Zone of SW Japan, were described by combining EPMA and LA-ICP-MS analytical data. This was done in order to discuss the distribution of trace elements and REEs between minerals. Late Cretaceous granitoids of the Inner Zone occur in east-west zone with lateral extension of ca. 800 km on the west side of the Itoigawa-Shizuoka Fault [1]. Previous K-Ar dating and Rb-Sr dating for granitoids of the Sanyo Belt from the southern part of Hiroshima Prefecture yielded the ages of ca. 78-89 Ma [2, 3].

Two groups of granitoids of the Sanyo Belt were collected from pegmatite deposits in the Mihara Mine area (Hiroshima Prefecture) and in the Omishima Mine area of the eastern Geiyo islands (Ehime Prefecture), respectively. The other one from the eastern part of Takanawa Peninsula (Ehime Prefecture) was also examined in this study. Micro-textures on thin sections were observed by using EPMA (JXA-8800), and CHIME dating for monazites on the textures was performed by using the other EPMA (JCSA-733). Zircon grains, which were extracted from the rocks, were analyzed for the preliminary examinations for investigating U-Pb ages and chemical characteristics by using ICP-MS with femt-second laser. The 91500 Zircon Standard was used for this LA-ICP-MS study.

Several radioactive minerals such as monazite (the ideal formula CePO_4 , with LREEs, Y and Th etc.), zircon (ZrSiO_4), allanite [$(\text{Ca},\text{R})_2(\text{Al},\text{Fe},\text{Ti})_3\text{Si}_3\text{O}_{12}(\text{OH})$; $\text{R} = \text{Ce}, \text{Mn}, \text{La}, \text{Y}$ and Th], apatite [$\text{Ca}_5(\text{PO}_4)_3(\text{F},\text{Cl},\text{OH})$], xenotime (YPO_4) and thorite (ThSiO_4) were found commonly in some of the examined rocks from Mihara, Omishima and Takanawa. Titanite (CaTiSiO_5) was observed in others. On the basis of description in the present study, we confirmed that the amount of monazite is decreased remarkably with increase of allanite or titanite probably due to supply of Th and LREEs to these minerals.

The following micro-textures were described in the present EPMA study: the reaction of "monazite => zircon + thorite + allanite + apatite" (Mihara); (2) the assemblage of thorite + xenotime and the outer rim of anhedral to subhedral zircon (Takanawa); (3) euhedral zircon with negative crystal growth due to coexistence with thorite (Mihara). All of these textures imply the influence by hydrothermal metasomatism in the latest stage of plutonic magma process. The LA-ICP-MS study demonstrated the chemical characteristic that Th/U ratio of zircons from Mihara was decreased toward rim (i.e. core: 0.8-0.4; rim: 0.5-0.2 or less) due to breakdown of monazite in later stage. Together with this, Th, P and LREEs were supplied to thorite, allanite and apatite. This result suggests that the Th-U distribution in zircon is caused by element partitioning between phases but not the difference between metamorphic or igneous processes. On the basis of CHIME dating, we confirmed that the primary monazite in a pegmatite from Mihara formed at the late Cretaceous age of 81.7 +/- 6.4 Ma (error: 2 sigma). To discuss precisely the process of crystallization differentiation of this plutonic magma, additional zircon dating might be required.

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Keywords: radioactive mineral, trace element, rare earth element (REE), Inner Zone of SW Japan, late Cretaceous granitoids, pegmatite

Two types of spinel from a peridotite associated with Bushveld Complex, South Africa: Tectonic implications

Kazuyasu Shindo^{1*}, RAJESH, Hariharan M.¹

¹University of Johannesburg

Spinel is a common accessory mineral in ultramafic and mafic rocks, and because of its refractory nature, chemical composition of Cr-spinel is frequently used to infer the geotectonic environment of the rock which contains them. The tectonic setting of the largest layered ultramafic to mafic intrusion in the world, the Bushveld Complex, is still debated, with some studies suggesting a plume origin, while others arguing for a subduction setting. Few mineralogical studies have been carried out to address the possible tectonic setting. This study presents detailed petrographic and mineral chemical characterization of two types of spinels occurring within the Apiesdooringdraai peridotite, an extensive peridotite body that is spatially associated with the marginal sills and lower chill sequence, considered as parental to earliest magmas to the Bushveld Complex.

The peridotite body is composed mainly of olivine and orthopyroxene with minor amphibole, mica, spinel, apatite and sulphides. The first type of spinel is euhedral to subhedral and Cr-rich with Cr# ($=\text{Cr}/(\text{Cr}+\text{Al})$) of 0.58 to 0.78 and Fe# ($=\text{Fe}/(\text{Fe}+\text{Mg})$) of 0.60 to 0.75. With respect to the trivalent cations, the Cr-spinel grains do not show any within-sample variations. Mn and Ti are present in trace amounts. The second type of spinel is subhedral to anhedral and Al-rich with Cr# of 0.01 to 0.13 and Fe# of 0.25 to 0.34. Based on their petrographic and mineral chemical characteristics, the Cr-rich spinel is considered to represent the primary or near-primary spinel composition, while the Al-rich spinel is related to later fluid overprint contemporaneous with the formation of amphibole and mica in the rock. The later is further supported by the Ni and Zn contents in the Al-rich spinel, more than those in the Cr-spinel.

In comparison with a compilation of Cr-spinel composition from various tectonic settings, this study places constraints on the possible tectonic setting of the Bushveld Complex layered intrusion, forming part of the Bushveld large igneous province (Rajesh et al., 2013).

Reference

Rajesh, H.M., Chisonga, B.C., Shindo, K., Beukes, N.J., Armstrong, R.A. (2013) Petrographic, geochemical and SHRIMP U-Pb titanite age characterization of the Thabazimbi mafic sills: Extended time frame and a unifying petrogenetic model for the Bushveld Large Igneous Province. *Precambrian Research* (in press).

Keywords: Cr-spinel, peridotite, Bushveld complex, tectonic setting

Textural and PGM characteristics of subarc podiform chromitite xenoliths from Takashima, southwest Japan

Makoto Miura^{1*}, Shoji Arai¹

¹School of Natural system, Kanazawa University

The chromitite xenoliths from Takashima alkali basalt, the Southwest Japan, represent current subarc chromitites, possibly of podiform type in terms of the occurrence, mineral chemistry and textures (Arai and Abe, 1994). We found laurite, one of PGM (platinum-group mineral), and pentlandite in the Takashima chromitite. The finding is the first report on the occurrence of PGM from chromitites as xenoliths to our knowledge.

Laurite was commonly found as minute (<5 microns across) solitary grains of euhedral shape embedded in chromian spinel. Sometimes, very fine (around 1 micron) grains of Cu-bearing pentlandite are associated with the primary silicate mineral (mainly pyroxenes) inclusions in spinel. Chondrite-normalised PGE pattern of the Takashima chromitite shows a slightly negative slope from Ru to Pt, which is analogous to that of some podiform chromitites from ophiolites, such as the Oman ophiolite. In addition, laurite is one of most common PGM in podiform chromitites from ophiolites (Ahmed and Arai, 2003).

The textures (layered, massive, schlieren, unti-nodular and rarely nodular texture) of Takashima chromitites (Arai and Abe, 1994) are analogous to that of some chromitite from ophiolite, especially the Oman ophiolite. Spinel in Takashima chromitite show a relatively high Cr# (= Cr/(Cr+Al) atomic ratio), 0.6 to 0.8, and a low TiO₂ content, 0.16 to 0.63wt% (Arai and Abe, 1994). Spinel in Rajmi discordant chromitite, Oman, also show a similar high Cr#, 0.75 to 0.78, and a low TiO₂ content, 0.15 to 0.2wt%. Both the Takashima and Oman chromitites are comparable in the spinel chemistry with some arc-related plutonic rocks (Arai et al., 2011). This indicates that some of the podiform chromitites from ophiolites, including those from the Oman ophiolite, are of subarc origin.

Keywords: laurite, PGM, chromitite xenoliths, Takashima, subarc chromitite

Significance of Fe-Cu-Ni-sulfide inclusions in plagioclase megacrysts from Japan

Takuya Echigo^{1*}, Shino Nishimagi², Mitsuyoshi Kimata², Masahiro Shimizu², Shizuo Saito², Norimasa Nishida², Mihoko Hoshino³

¹Shiga Univ., ²Univ. of Tsukuba, ³AIST

Anorthite megacrysts, which are high-calcic plagioclase ($An > 90$ mol%) phenocrysts larger than 10 mm, are characteristic minerals occurring in basalt - andesite from Japanese Islands arc (Kimata et al. 1995). Anorthite megacrysts from Miyake-jima contains various inclusions such as native copper (Cu: Murakami et al. 1991), native zinc (Zn: Nishida et al. 1993) and native brass (Zn-Cu alloy: Nishida et al. 1993). In addition, hydrocarbon was also reported from Miyake-jima anorthite (Kimata et al. 1993), which suggests that slab sediments on subducting plates had important role for crystallization of these anorthite megacrysts. These past studies indicate that mineral, melt or liquid inclusions in anorthite megacrysts may afford a clue to the formation process of such minerals.

We report the analytical results of sulfide inclusions in anorthite megacrysts from Ogi peninsula in Sado Island and Mt. Fubou (one peak of Zao mountains). Both megacrysts occur in lavas erupted in the Tertiary period; the former volcano is located along the volcanic front and the latter is along the back-arc in Japan, respectively. The chemical analyzes of the anorthite megacrysts (host crystal) and sulfide inclusions were carried out using an electron microprobe analyzer with wavelength dispersive X-ray spectroscopy (EMPA-WDS: JEOL JXA-8621) and/or a scanning electron microscope with energy dispersive X-ray spectroscopy (SEM-EDS: JEOL JSM-6610LV).

The analytical results show that the anorthite megacrysts from both Ogi and Mt. Fubou contain sulfide inclusions that are droplet-shaped and 30 - 50 micrometer in diameter. The chemical compositions of the sulfide inclusions from both of the localities are heterogeneous; Fe-rich phase and Cu-rich phase were observed within a single inclusion. Quantitative analyzes suggest that the Fe-rich phase is pyrrhotite [$Fe_{(1-x)}S$ ($x=0-0.17$)] and Cu-rich phase is cubanite ($CuFe_2S_3$), respectively, and these phases contain both Ni and Cu. These sulfide inclusions consisting the two phases may be trapped as fluid inclusions in the host crystals (anorthite megacrysts) at high temperature. The trapped sulfide liquids seem to be separated from silicate melts as monosulfide solid solution ($Fe_{(1-x)}S-Ni_{(1-x)}S$: Naldrett et al. 1967) or intermediate solid solution ($CuFeS_2$: Fleet 2006) and exsolved into pyrrhotite and cubanite in the host crystals upon cooling. The present study indicates that sulfide melts rich in Fe, Cu and Ni were generated within magmas along the volcanic front and back-arc in Japan.

Keywords: Plagioclase megacryst, Arc magma, Sulfide, Inclusion

A novel micro-XRD technique for the selected area in petrographic thin section using FIB and high-sensitive XRD

Sayako Inoue^{1*}, KOGURE, Toshihiro¹

¹Earth & Planetary Sci., Univ. Tokyo

Powder X-ray diffraction (XRD) is the most common and convenient technique for determining mineral compositions in rock or crystal structure of minerals. However, they can be heterogeneous within a rock or petrographic thin section and conventional XRD is often useless because it requires a considerable volume of the specimens. To overcome this problem, so called micro-XRD instruments have been developed and applied. Especially recent confocal X-ray mirror can generate a convergent X-ray source whose brightness close to synchrotron radiation. Two-dimensional X-ray detectors such as CCD camera and imaging plate (IP) are also useful to acquire diffracted X-ray efficiently. On the other hand, micro-sampling techniques using a focused-ion-beam (FIB) developed mainly to prepare TEM specimens can select and pick up minute mineral fragments from interested areas in petrographic thin section. Although the maximum size to pick up using FIB micro-sampling is rather limited, it can be compensated by the bright X-ray source and efficient XRD detectors. We will report the application of these techniques assembled to determine the crystal structures of chlorite and related minerals in petrographic thin section.

Chlorite, one of the most abundant phyllosilicates found in variety of geological environment, has six polytypic groups. Like other phyllosilicates, the detailed investigation of its crystal or stacking structure is crucial. 'Chlorite-like minerals' (chlorite, serpentine, and their interstratification) from Toyoha geothermal system, southwestern Hokkaido, Japan was investigated using this novel micro-XRD, as well as electron diffraction and high-resolution imaging in TEM. We found that chlorite-like minerals in veins and matrices are different (mainly serpentine in the veins and chlorite in the matrices) from micro-XRD pattern. Polytypic groups of chlorites in the matrices seem to be dependent on their chemical compositions.

Keywords: XRD, FIB, petrographic thin section, HRTEM, phyllosilicate, chlorite

Collision Synthesis of Fe-based Complex Oxides with High Temperature and High Pressure Phase by High-Speed Ball-Milling

Takeshi Hashishin^{1*}, Zhenguan TAN¹, Kazuhiro YAMAMOTO¹, Nan QIU¹, Satoshi OHARA¹

¹Osaka University

1. Research Background

Mechanochemical grinding of powder with micro-order in diameter is suitable to be fine by general planetary ball-milling process (Ohara et al., 2008). The centrifugation with high gravity such as 150 G can realize the high collision between steel balls, which is mainly composed of shear stress between them, induced by high-speed ball-milling. In our previous study, a mechanochemical approach inspired by the Allende meteorite (Smith et al., 1981) to produce sophisticated carbon nanomaterials is reported (Ohara et al., 2010; Tan et al., 2010). It is demonstrated that unique carbon nanostructures, including carbon nanotubes, carbon onions, and new carbon nanorings are synthesized by high-speed ball-milling of steel balls. The carbon nanorings have the diameter of several ten nanometers observed by atomic force microscope (AFM). It is considered that the gas-phase reaction takes place around the surface of steel balls under local high temperatures induced by the collision energy in ball-milling process, which results in phase separated unique carbon nanomaterials. This mechanochemical effect can be also applied to synthesis Fe-based complex oxides (Ohara et al., 2010).

In this study, ilmenite was synthesized via collision-shock by high-energy ball-milling process and the existence of ilmenite with high temperature and high pressure phase was clarified from analytical measurement based on the diffraction patterns: selected area diffraction patterns and ultrahigh-resolution images.

2. Experimental Procedure

The raw material was commercially available TiO₂ (ST-01, Ishihara Sangyo, Japan) with a mean particle size of 7 nm, which was calculated from the specific surface area (SSA). TiO₂ nanoparticles with a volume of 10 cm³ were loaded into a 180 cm³ cylindrical vial along with 50 cm³ milling balls. The milling balls were commercial stainless steel balls of SUS440C with a 3mm diameter. Mechanochemical treatment was performed by a high-speed ball-milling apparatus (High-G, Kurimoto Ltd., Japan) that operated for 3 h in an air atmosphere under centrifugal forces of 150 G. The phase evolution of the milled nanoparticles was characterized by X-ray diffraction (XRD; Ultima IV, Rigaku, Japan) using Ni filtered Cu-Kalpha radiation.

3. Results and Discussion

Figure 1 shows the XRD patterns of raw powder (a), and products as-milled at 150 G for 3 h by using stainless steel balls of SUS440C (b). The patterns of Fig. 1 (a) were assigned to anatase compared to the inorganic materials database of XRD patterns (supplied by NIMS atom work). The patterns of Fig. 1 (b) were assigned almost to ilmenite except iron peaks. Generally, ilmenite is formed at more than 1200 °C by solid-state reaction (Grant et al., 1972). It was suggested that the temperature inside stainless steel pot had risen locally to more than 1200 °C via higher impact energy induced by collision between balls of SUS440C. Interestingly, high temperature and high pressure phase of Fe₂TiO₄ was co-existed with Fe-rich ilmenite (Fe_{1.5}Ti_{0.5}O₃) and stoichiometric ilmenite (FeTiO₃) near 2 theta region ranging from 32 to 34°. In addition, the 2theta value of Fe₂TiO₄ was extracted from the literature (Nishio-Hamane et al., 2012).

Keywords: High-speed ball-milling, Collision synthesis, Fe-based complex oxides, High temperature and high pressure phase

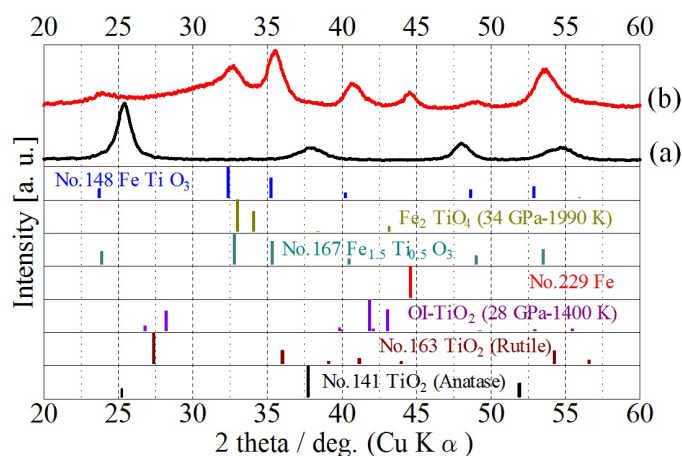


Fig.1 XRD patterns of raw powder (a) and product formed at 150 G for 3 h by using stainless steel balls of SUS440C (b).

Paleomagnetic age dating of the White Pine Cu mineralization, northern Michigan, U.S.A.

Kazuo Kawasaki^{1*}, SYMONS, David², DIEHL, Jimmy F.³

¹University of Toyama, ²University of Windsor, ³Michigan Technological University

Paleomagnetic results are reported for the White Pine stratiform sedimentary copper (SSC) mineralization, northern Michigan, U.S.A. Paleomagnetic analysis of 176 specimens (19 sites) using mostly thermal step demagnetization isolated collinear characteristic remanent magnetization (ChRM) directions in both magnetite and hematite in both the SSC zones and overlying pyritic and upper zones of the Nonesuch Formation. A paleomagnetic fold test is positive, showing that the normal-polarity ChRM is pre-folding in origin. There is no statistically significant difference at 95% confidence between the tilt-corrected paleopoles for the SSC zone and the overlying unmineralized host rocks of the pyritic and upper oxidized zone of the Nonesuch Formation, indicating that the SSC mineralization is co-eval with host rock oxidation. Combining the ChRM directions from this study and from Henry et al. (1977) gives a paleopole at 7.3°N, 174.7°E (N = 29, A₉₅ = 3.0°) for the SSC mineralization and nonmineralized host rocks sites, yielding an age of 1063±8 Ma on the Keweenawan Apparent Polar Wander Path. Thus the observed paleomagnetic age is likely to date both the average age of oxidation and mineralization of the SSC zone, supporting the need for gravity-driven recharge of subsurface brines by meteoric water from adjacent highlands to supply the epigenetic oxygen and copper to form the White Pine deposit.

Keywords: Paleomagnetism, Ore Genesis, Stratiform Sedimentary Copper, Mesoproterozoic, U.S.A.